MAGNETITE AND ILMENITE OF WESTLAND BEACHES : ANALYTICAL STUDIES BEARING ON THEIR SOURCES AND ACCUMULATION PATTERNS

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Chew Pok Min 12.3.81

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ABSTRACT

The extensive accumulations of black sands along the beaches of the West Coast of the South Island contain ilmenite and magnetite. In the Jackson Bay - Haast area magnetite predominates, but to the north the sands are ilmenite-rich. It has been established that throughout the entire region both the ilmenite and magnetite have been derived from the schists behind the Alpine Fault.

Ultramafic sources near, or within the schists (Red Mountain in South Westland; Pounamu ultramafic pods in northern Central Westland) provide a small amount of chromium-rich magnetite, and because of this, the minor element contents of magnetite have been particularly useful in providing evidence on dispersion and beachsand accumulation patterns of magnetite from the hinterland source rocks.

Regional variations in the composition of the Alpine Schist are reflected in the detrital heavy mineral assemblages of sediments from the schist-draining rivers. Schists of South Westland differ from those to the north in releasing more magnetite and hornblende, but less ilmenite, biotite and garnet.

Because equilibrium has been attained between the various minerals within broad regions of the schists, magnetite and ilmenite samples from specific schist zones reflect the natural distribution of first-row transistion elements between the crystal lattices of these two oxide minerals. Samples of detrital magnetite and ilmenite from Tuhua Granites, however, appear to indicate considerable

local variations within these rocks.

The analytical work includes a critical examination of methods for dissolving magnetite and ilmenite for Atomic absorption. The procedures used minimise interelement interference effects and enabled any small correction to be made.

CHAPTER I

INTRODUCTION

General

Along the West Coast beaches of the South Island of New Zealand it is a striking characteristic that a more or less continuous ribbon of blacksand accumulates at the high tide mark. These sands comprise heavy detrital minerals consisting mainly of ilmenite and magnetite. Moreover, in many places there are heavy localised accumulations in sheltered bays or in the dune sands. It is clear that these heavy minerals must have been derived from the hinterland rocks. In places, as for example at Barrytown and in the Cape Foulwind area, the exploitation of the ilmenite for its titanium content has been seriously considered and at many localities beachsands have been worked for their gold content.

In Westland the present coastline lies more or less parallel to the Alpine Fault behind which the Alpine Schists rise steeply on the western flank of the Southern Alps. To the east of the Fault the metamorphic rocks grade back from garnetiferous feldspathic schists through progressively lower grade zones into the non-schistose greywacke and argillite that comprise the Torlesse series (Mason, 1962). Although the position of the zone boundaries is not well defined in some places, it is clear that these zones form structurally simple bands sub-parallel to the Fault. On account of the closeness of the Main Divide to the coast, many westward flowing rivers are short and rapid. This, together with the high erodibility of the schists, the high precipitation and heavy outflow of water in the rivers,

means that large detrital loads are moved rapidly down-river to the coast (Appendix 1). It is a reasonable inference that the heavy beachsand minerals have been derived from the rapdily eroding Schists in which they occur as accessory constituents. Nevertheless, it is perhaps a little surprising that there has been so little work having a direct bearing on actual beachsand accumulation relative to the sources of supply.

The combination of geological and geographical features of Westland provides an attractive situation for undertaking a correlative study of the accumulating blacksands and the sediments coming down the rivers. However in the northern region of Central Westland the situation may have been somewhat complicated by the significant outcrops of granites between the fault line and the coast, since these also supply detrital materials to the beaches (Bradley et.al. 1979). Furthermore there are massive morainic tongues often extending to the coast, but the courses of the present-day rivers are rather stable and the contribution from these moraines to the bed loads must be small as compared with the supply of detritus from denudations of the Alpine rocks. Some supply of detritus from these moraines could occur from marine erosion of their coastal bluffs. In addition there are also effects arising from longshore drift from the south (Carter, 1975) and from variations in sea-level during periods of glaciation.

As to previous work, particular reference should be made to the classic mineralogical studies carried out by Hutton (1950). In this extensive work the author made detailed studies of the sand size minerals present

in dredge-concentrates as well as river and beachsand samples, but the research was not directed towards establishing mineral provenances. More recently Bradley et.al. (1971) made a different type of survey on the sources and persistence characteristics of detrital heavy minerals supplied by the Tuhua granites and the Haast schists within the Taramarau catchment. Information on the proportions of ilmenite and magnetite in areas where there are particularly large concentrations have been gathered by Nicholson et.al. (1958), Nicholson (1967), McPherson (1978) and by the Carpentaria Exploration Company (reports submitted to the Mines Department).

Important petrological work having a bearing on the problem has been carried out by Reed (1958) who performed bulk rock chemical analysis and detailed mineralogical study on the various metamorphic zones (mainly to the north), by Mason (1962) who examined mineral transformation within the successive metamorphic zones of the Alpine Schists and by Cooper (1971) who described the progressive mineralogical changes in the meta basic schists in the Haast River rocks.

The present work can be considered in some respects as an extension of the work done by Bradley, whose investigations are described in an earlier University of Canterbury thesis (1977). There are, however, important differences. The present work does include a reconnaissance mineralogical survey of the heavy river and beachsand minerals from Martins Bay northwards, but there is an emphasis on the chemical analysis of the content of minor elements in the magnetite and ilmenite fractions obtained as systematically as possible from various

localities over the whole region. The minor elements include Ti, V, Cr, Mn, Ni, Zn, Cu and Mg.

As work progressed it became evident that two points of particular relevance in tracing the movement of river sediments and beachsands were :

(i) The geographical variations of the ratio of ilmenite:magnetite within the sample; and

(ii) the chromium content of magnetite.

The first point is significant because there are regular variations in the ratios for beachsands and river sediments from south to north. The chromium content is particularly important because a proportion of the magnetite in the Jackson Bay area is derived from ultramafic rocks which are invariably rich in chromium. The known ability of the magnetite lattice to concentrate chromium means that the magnetite from this source is rich in the metal. The dispersion and dilution of this magnetite with this built-in chemical indicator prove easy to follow in South Westland. Again, in North Central Westland, a proportion of the magnetite carried by the rivers (Waitaha to Taramakau) is derived from the Pounamu ultramafic lenses which have been mapped within the schists (Guyon, 1967). Therefore, in this area too the dispersion of the chromium-rich magnetite along the beach can readily be followed on the basis of chemical analysis.

Aspects of work

An important initial aspect of this work lay in the evaluation of methods for chemical analysis of magnetite and ilmenite. These are described in Chapter II dealing with laboratory methods generally.

As regards discussion on beachsand accumulation

patterns, the region is conveniently divided into three sections covering the region from south to north (to provide for possible transport effects arising from longshore drift towards the north).

(i) Jackson Bay-Haast area where ilmenite: magnetite ratios are low.

(ii) Central Westland region extending from the Paringa River northwards to the Waitaha, where ilmenite:magnetite ratios are higher.

(iii) North Westland beaches where there is a proportion of chromium-rich magnetite derived from the Pounamu ultramafic pods (within the schists of this northern region). It happens that this enables the movement of these magnetites to the north along the Paparoa Coast up as far as Cape Foulwind to be readily traced.

Finally the availability of information on the minor element content of magnetite and ilmenite from rocks over this region does enable discussion of some underlying geochemical features. This information is of value in relation to the schists, on which there appears little information.

CHAPTER II

SAMPLE HANDLING AND LABORATORY PROCEDURE

I FIELD COLLECTION

Sand samples were obtained from most of the major rivers and accessible beaches within the Westland region. Some of the South Westland and most of the Taramakau samples had been collected by Bradley (M.Sc.thesis,1977). His North Westland samples were mainly taken from headwaters of small feeder streams so as to ensure sampling from small areas. In connection with this work a good many other samples were collected to provide a more complete coverage.

The beach samples were mostly taken from the dry sand about the high tide mark. These were firstly passed through a field sieve of either 0.5ϕ (750 micron) or 1ϕ (500 micron) mesh size depending on the proportion of fine sand available. Up to 5 kilogram of the fine sand was collected as necessary. Sample bags were coded and the locality carefully marked on a map. Wherever possible river samples were taken from dry sandbanks, again with sieving where practicable. The use of a gold pan helped in concentrating the heavy minerals.

Magnetites from river sediments and the beachsands were concentrated and collected as required with a hand-magnet. The river-borne magnetite was more tedious to collect since it accumulated under lighter gravels and behind small rocks. Beachsand magnetite, however, was easily separated by simply passing the hand-magnet over the sand.

II LABORATORY PROCESSING

In the laboratory the dried field samples were separated with a mechanical siever into 1ϕ, 2ϕ, 3ϕ, 4ϕ and <4ϕ sieve mesh fractions (see Appendix 2 for ϕ connotations). While in principle it would have been desirable to float all the sieve fractions, those coarser than 3ϕ tended to contain increasing properties of grains with inclusions and composite grains which would complicate magnetic separation and chemical analysis. Attention was therefore paid to the 3ϕ and 4ϕ fractions, but wherever these were in short supply the coaser fractions were also judiciously processed.

The cuts were floated in tetrabromoethane (T.B.E.) or bromoform to concentrate the heavy minerals from the lighter materials comprising mainly feldspars, quartz and composite rock fragments (see Table 2:1). While about 250 grams was the usual weight of each cut subjected to floatation , the weight was varied according to the proportion of the heavy minerals present. After thorough washing with absolute alcohol and petroleum ether, the heavy mineral fraction was oven-dried and its weight determined. Magnetite was then removed with a hand-magnet wrapped in a plastic sheet to facilitate removal of magnetite from the magnet. Through repeated passage of the magnet over the thinly spread sample, magnetite of purity greater than 95% (as checked by optical examination) could be obtained. Weight of the magnetite was recorded to provide quantitative data. Field concentrated magnetites were firstly washed, dried and sieved to obtain the 3ϕ and 4ϕ cuts and subsequently cleaned as above.

TABLE 2 : 1

Densities of Heavy Floatation Liquids and more Common Minerals

Mineral	Density (g/cc)
Feldspars	2.5 - 2.7
Quartz	2.65
Muscovite	2.76 - 3.1
Biotite	2.7 - 3.2
Bromoform	2.76
Tetrabromoethane	2.96
Hornblende	3.2
Apatite	3.27
Methylene iodide	3.34
Epidote	3.35 - 3.45
Garnet	3.4 - 3.5
Zircon	4.67
Ilmenite	4.7
Magnetite	5.18
Cassiterite	6.8 - 7.1

The remainder of the heavy mineral concentrate was then passed through the Franz isodynamic magnetic separator set at 8^{o} side slope, 15^{o} forward tilt using successively ·2, ·35, ·45, ·75 and 1·2 amperes (A) (Baker, 1962). The weight of each fraction was recorded.

Ilmenite was predominately present in the ·2A magnetic cut. With the aid of a binocular microscope and making comparison with a "percentage estimation chart" (see Appendix 3) the percentage of ilmenite in the ·2A cut was estimated. Occasionally grain-counts were made to cross-check the estimation. Thus, together with the recorded weight of the ·2A cut, the weight of ilmenite in the sample could be calculated.

In order to provide ilmenite samples as pure as possible for chemical analysis, the ·2A magnetite fraction was again floated in methylene iodide and then repeatedly passed through the magnetic separator operated at 20^{o} side slope, 15^{o} forward tilt and ·25A with a feed rate of 10-15 grams per hour (Marshall et.al., 1958). Purification of ilmenite samples to greater than 90% (as checked by optical examination) could easily be achieved on beachsand material in which the grains were usually rounded. A different setting was required for some river samples, particularly those collected at the headwaters. This was probably because these grains tended to be angular, bladed or tubular and their shapes inhibited their traverse up the 20^{o} side slope. This was remedied by operating the magnetic separator at 15^{o} forward tilt, ·2A and varying the side slope by trial between 8^{o} and 15^{o}. It could be mentioned that while most river samples had to be floated to concentrate the ilmenite, some black ilmenite-run beachsands could be

fed directly into the separator to obtain the ilmenite without prior floatation.

In principle, the differences in mineral densities should allow their purification through the use of a "superpanner". This was explored but found to be less satisfactory than the Franz separator in terms of time, effort and mineral purity.

III METHODS OF CHEMICAL ANALYSIS

(a) Decomposition of magnetite for Atomic Absorption Spectrophotometric Analysis (AAS).

Of all the possible methods the AAS method was chosen for the analysis of magnetite because of its high sensitivity for the elements of concern and the ease of determining many elements from the same solution. Furthermore, it is rapid and the sample size required is small. The method requires that all samples be brought into solution but this is no particular disadvantage as far as magnetite is concerned because it is readily soluble in concentrated hydrochloric acid.

On the other hand it is necessary to approach the AAS method with caution. It was important to check on interferences from iron in particular and from the amount of hydrochloric acid required to dissolve the sample.

Procedure

The magnetite was finely ground using an agate mortar. Approximately ·5 gram of the powder was accurately weighed into a 7·5 cm evaporating dish. Between 20-30 mls of AR hydrochloric acid were added and the dish was heated on a steam-bath for 3-4 hours with small addition of acid when necessary. When the black solid had disappeared,

the acid was allowed to evaporate off completely.

Then exactly 2·5 ml of AR hydrochloric acid (see pp 14) was added to redissolve the residue. Invariably a small amount of paler residue remained. The resulting solution was filtered and washed through a No.4 sintered glass crucible and finally transferred to a 25 ml volumetric flask. The solution was made up to the mark with distilled water. Any undissolved residue was dried and its weight was subtracted from the initial weight of magnetite. In some cases where only smaller amounts of the sample were available, ·2 gram samples were decomposed in the appropriate volume of acid and finally prepared in 10 ml volumetric flasks. All sample solutions were prepared in duplicate.

Nature of acid insoluble residue

The undissolved residues representing between 1-10 percent of initial magnetite weights were generally whitish although a few samples such as SW24, SW27, CPM11 were greyish to brownish black in colour. Examination under the microscope showed the presence of quartz, and smaller amounts of sphere, epidote, feldspars and occasionally chromite or ilmenite were identified by x-ray diffraction (XRD). It is considered that the residue was probably derived from composite magnetite grains and any contamination that escaped removal during purification of magnetite.

X-ray fluorescence scans on the residue for the elements under study showed that, with the exception of titanium, probably derived from the small amounts of sphere, the other elements,if present at all,were in very minor amounts. This confirmed that the elements of particular concern in the analysis had passed into the solution quantitatively.

Study of Interferences in AAS Analysis

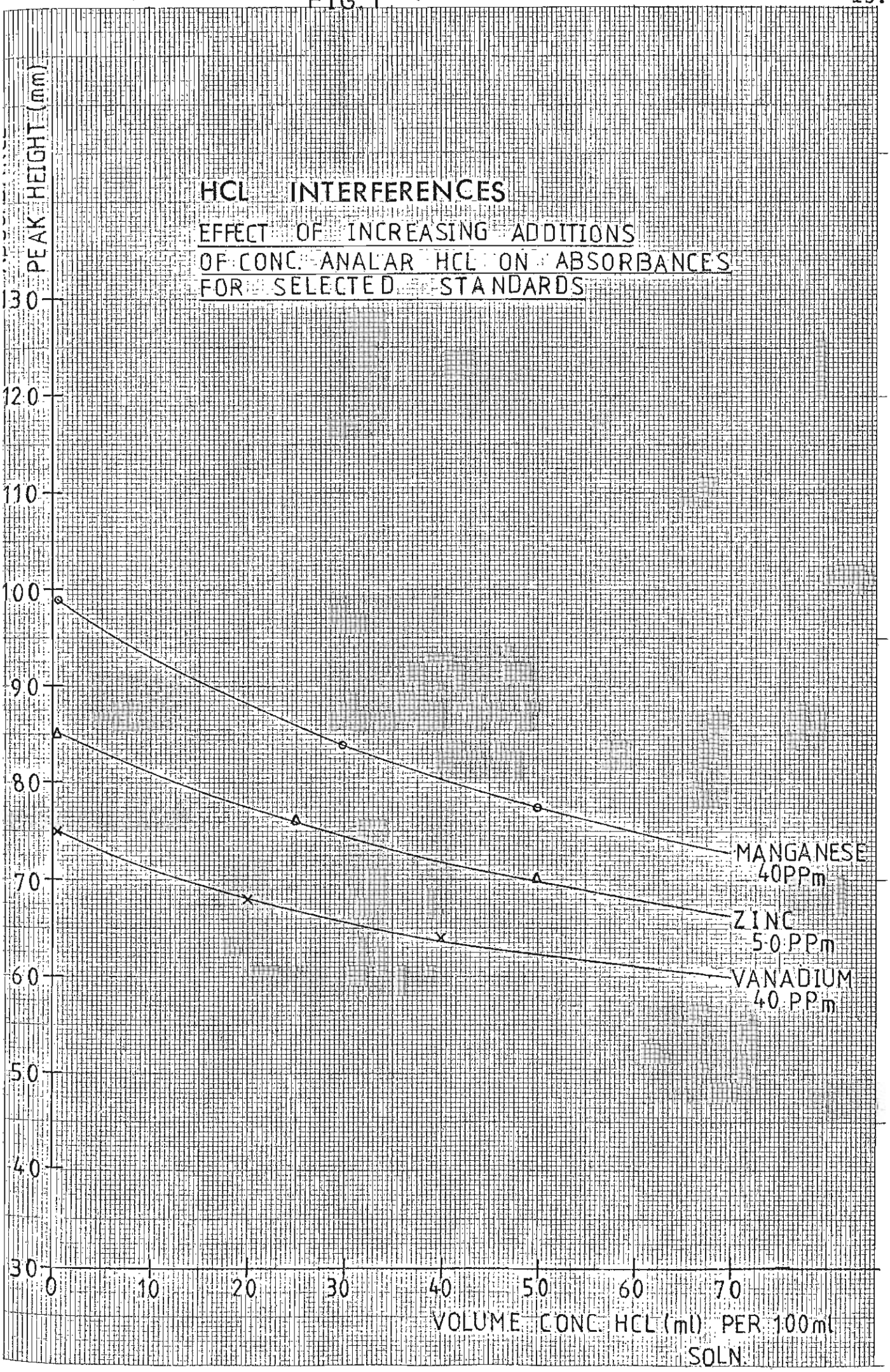
Govett and Whitehead (1973) in their investigation of some transistion elements in geological materials found that errors in AAS determinations of Pb, Zn, Ni, Co may occur due to the presence of large quantities of Fe, Al, Ca, Mg, Na and K in the sample solution. In analysing for the minor elements in magnetite, the possibility of interference from the high iron content and from hydrochloric acid was also examined. The findings were in close agreement with those reported by Lovelock (unpublished B.Sc. (Hons.) report, 1978).

Effect of Hydrochloric Acid

This was investigated by a study of the effect of adding successively larger volumes of concentrated AR hydrochloric acid to selected standards of the element.

The results for three elements (Vanadium, Manganese, Zinc) are summarised in graphs (Fig. 1). It can be seen that for the three elements tested, successively higher concentrations of hydrochloric acid depress their absorbances non-linearly. In principle, all the other elements of concern should be tested similarly but since an interference effect was already apparent for these three elements, it was decided to control the situation for all elements by working with sample solutions of constant acidity. For this reason it was necessary firstly to evaporate all sample solutions to dryness and then redissolve in 2·5 mls of concentrated hydrochloric acid as described on pp.(13). This volume of acid was used because it was sufficient to redissolve the residue. The calibration solutions of course would be prepared to the same acid concentration, i.e. 1M hydrochloric

FIG. 1


HCL INTERFERENCES
EFFECT OF INCREASING ADDITIONS OF CONC. ANALAR HCL ON ABSORBANCES FOR SELECTED STANDARDS
PEAK HEIGHT (mm)
130
120
110
100
90
80
70
60
50
40
30
0
10
20
30
40
50
60
70
VOLUME CONC. HCL (ml) PER 100ml SOLN.
MANGANESE 40PPm
ZINC 5·0 PPm
VANADIUM 40 PPm

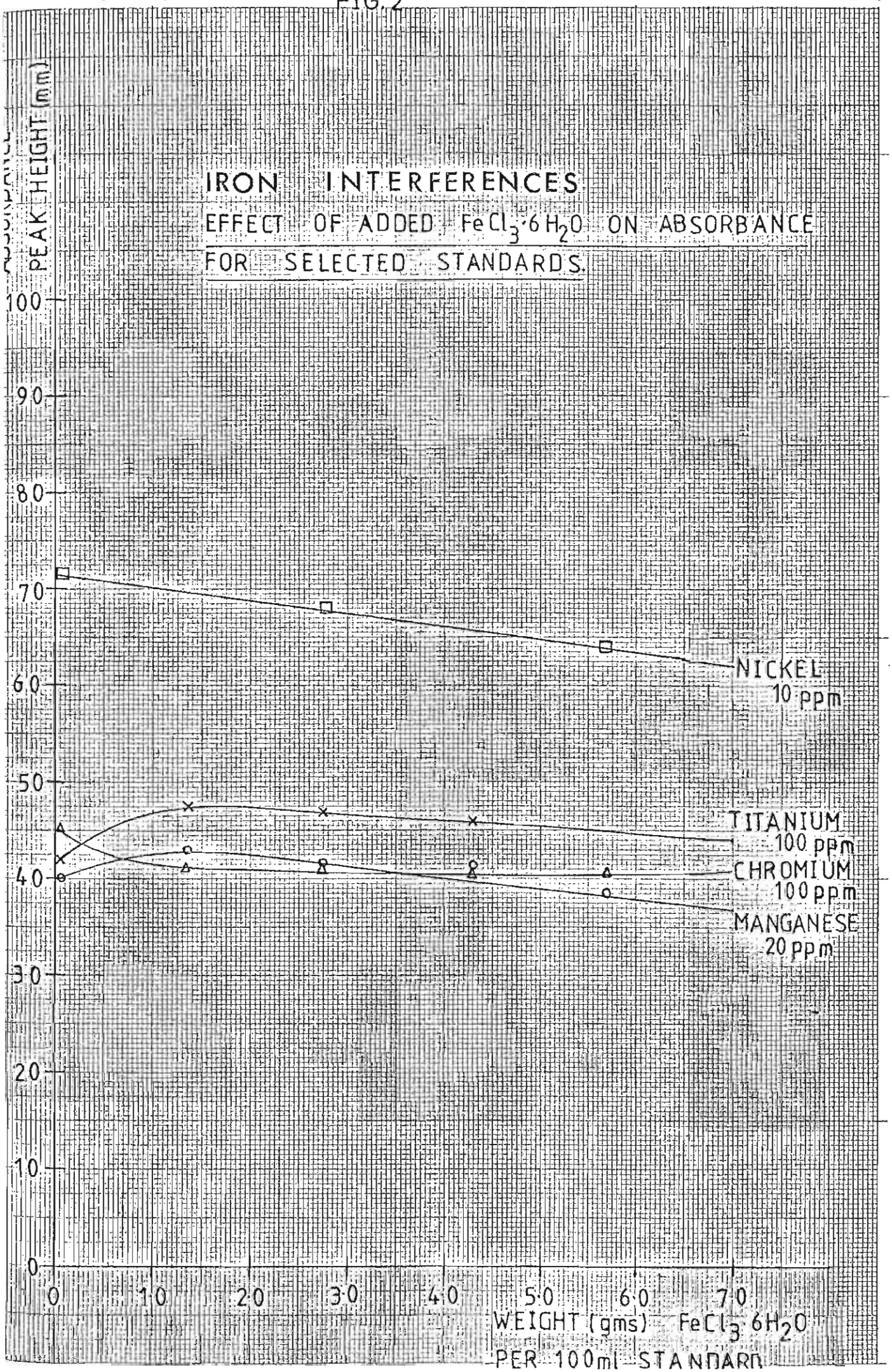
acid. Any influence of varying acid and chloride ions concentration on the atomic absorption response was thereby avoided.

Effect of Iron

To test the effect of large quantities of iron on the atomic absorption measurement of minor elements, "Merck"ferric chloride was used as the iron source. Its purity was such that the elements under study, if present, were low and compensation for them was easily made by taking measurements on blank solutions that contained ferric chloride only. An iron compound such as AR ferrous ammonium sulphate was not used because it contained NH_4^+ and SO_4^{2-} in solution which could introduce additional interferences. Ferric chloride contained only Fe^{3+} and Cl^- which provided a situation similar to a solution of magnetite dissolved in hydrochloric acid.

The investigation involved adding to a selected standard of an element varying amounts of ferric chloride; 1·4, 2·8, 4·2, 5·6 grams in 100 mls corresponding stiochiometrically to 0·1, 0·2, 0·3, 0·4 grams of magnetite in 25 ml. The absorbances of these solutions were compared with that of the standard of the same concentration to which iron had not been added

FIG. 2


IRON INTERFERENCES
EFFECT OF ADDED $FeCl_3 \cdot 6H_2O$ ON ABSORBANCE
FOR SELECTED STANDARDS.
PEAK HEIGHT (mm)
100
90
80
70
60
50
40
30
20
10
0
NICKEL
10 ppm
TITANIUM
100 ppm
CHROMIUM
100 ppm
MANGANESE
20 ppm
0
10
20
30
40
50
60
70
WEIGHT (gms) $FeCl_3 \cdot 6H_2O$
PER 100ml STANDARD

The results of tests for titanium, nickel, chromium and manganese are summarised in Fig. (2). Iron interferences are found to be different for the different elements under analysis. The following points may be noted :

1. Chromium exhibited a depression that remained reasonably constant regardless of the amount of ferric chloride added.

2. Nickel showed a depression proportional to the amount of iron added.

3. Titanium and Manganese exhibited an initial enhancement which gradually fell off with increasing concentration of ferric chloride.

4. Both Zinc and Copper (not plotted on figure) did not show significant interference effects from added iron.

These tests indicated that for zinc and copper, interference from iron was negligible, but for titanium, chromium, manganese and nickel the interferences could not be ignored. To simplify the iron compensation procedure, it was necessary to have a constant iron concentration in all sample solutions. For this reason magnetite samples of .5g or .2g only were prepared to a final volume of 25 ml and 10 ml respectively as described on pp. (13). The calibration solutions for all other elements except zinc and copper would be added an equivalent amount of iron in the form of ferric chloride, i.e. 7g ferric chloride in 100 ml of standard solution.

There is no evidence in the literature on inter-elemental interference of minor amounts of element. Since most elements under study are present in only minor amounts,

inter-elemental interference, if present at all, would be small and could be confidently ignored.

Standard solutions

With the exception of titanium, the stock standard solutions were prepared according to the AAS Varian Techtron Manual (see Table 2:2). In the case of titanium, AR potassium titanium oxalate was used in place of titanium metal. The oxalate is more readily available, and it is stable and soluble.

As a guide to the concentration ranges to be covered in calibration for each individual element, data on magnetite composition quoted in Deer, Howie and Zussman (Vol.5, 1963) were most useful. As far as possible the concentration ranges of the standard solutions were prepared to cover all the sample solutions. However, for solutions that showed concentrations outside the calibration range, they were diluted with 1M hydrochloric acid. It must be noted that dilution would reduce the iron concentration in the sample solution and probably cause some deviations in results when compared with iron-compensated calibration solution, but the effects were sufficiently small not to warrant any recalibration.

The flame types and general operating conditions adopted for analysing the elements with the Varian techtron AA5 spectrometer are shown in Table 2:3.

Calculations

From the calibration graph of the standards, there was obtained for each sample, a direct value of the concentration in parts per million (ppm) of the element in the sample solution.

TABLE 2 : 2

Preparation of STOCK STANDARD SOLUTIONS

ELEMENT	STANDARD CHEMICAL	SOLUTION TECHNIQUE
Titanium	AR Potassium titanium oxalate $K_2TiO(C_2O_4)_2 2H_2O$	Dissolve 14.79g Pot. titanium oxalate in 2% H_2SO_4 and make up to 1000 ml with 2% H_2SO_4 to give 2000 µg/ml Ti
Vanadium	AR Ammonium metavanadate NH_4VO_3	Dissolve 2.296g ammonium metavanadate in 1M.HCl and make up to 1 litre with 1m HCl to give 1000 µg/ml V.
Chromium	AR Potassium tichromate $K_2Cr_2O_7$	Dissolve 5.660g of Pot.dichromate in 1:1 HCl. Dilute to 1 litre to give 2000 µg/ml Cr.
Manganese	Manganese strip 99.9%	Dissolve 1.000g manganese in minimum volume 1:1 nitric acid and dilute to 1 litre to give 1000 µg/ml Mn.
Nickel	Nickel strip 99.9%	Dissolve 1.000g nickel in 1:1 nitric HNO_3 and dilute to 1 litre to give 1000 µg/ml Ni.
Copper	Copper strip 99.9%	Dissolve 1.000g of copper in minimum volume of 1:1 HNO_3 and dilute to 1 litre to give 1000 µg/ml Cu.
Zinc	Zinc foil 99.9%	Dissolve 1.000g of zinc in 40ml 1:1 HCl and dilute to give 1000 µg/ml Zn.
Magnesium	Magnesium strip 99.9%	Dissolve 1.000g Mg in 1:4 nitric acid. Dilute to 1 litre to give 1000 µg/ml Mg.

TABLE 2 : 3

OPERATING CONDITIONS USED ON VARIAN TECHTRON AA5 SPECTROMETER

ELEMENT	CURRENT (MA)	FLAME TYPE	WAVELENGTH λ (nm)	FLAME STOICHIOMETRY
Titanium	10	N_2O/C_2H_2	364.3	Reducing Red cone ≃ 1.0 cm.
Vanadium	10	N_2O/C_2H_2	318.5	Reducing red cone ≃ 1.5 cm.
Chromium	5	N_2O/C_2H_2	425.4	Reducing
Manganese	5	N_2O/C_2H_2	403.1	Oxidising
Nickel	5	Air/C_2H_2	352.4	Oxidising
Copper	3	Air/C_2H_2	324.7	Oxidising
Zinc	5	Air/C_2H_2	213.9	Oxidising
Magnesium	5	N_2O/C_2H_2	202.5	Oxidising

The corresponding concentration of the element in the sample itself is given by

$$\frac{Cs \times V}{M} \quad \mu g/g \text{ (ppm)}$$

where Cs(μg/ml) is the concentration of the element in the sample solution, $V_{(ml)}$ the volume of the sample solution and M(g) is the mass of the magnetite that was taken into the solution.

(b) Decomposition of Ilmenite for Atomic Absorption Spectrophotometric Analysis (AAS)

In the literature there are two common methods described for the decomposition of the mineral ilmenite for chemical analysis. These are :

(i) dissolving in hydrofluoric-sulphuric acid mixture (HF/H_2SO_4), and

(ii) a pyrosulphate fusion method.

In this study both methods were evaluated and it was found that the pyrosulphate fusion method was more suitable for present purposes than the HF/H_2SO_4 method. This method is described below and the procedure for the HF/H_2SO_4 method together with a brief comparison of the two is given in Appendix (5).

The procedures used by O'Shaugnessy (1973) who was mainly interested in AAS determination of chromium content of ilmenite was in part followed with adaptation as outlined below.

Procedure

Three grams of AR potassium hydrogen sulphate were slowly heated in a small platinum crucible to expel water. To this 0.25 g of the finely powdered ilmenite sample was added and the crucible was heated with constant side to side rotation over an increasingly stronger flame. (See Fig. 3 a, b, c.).

When fusion was complete as shown by the absence of dark particles, usually after heating for 15-20 minutes, the crucible was heated as strongly as possible for a further 10-15 minutes. It was allowed to cool and then a further gram of potassium hydrogen sulphate was added, followed by reheating until a homogeneous melt was obtained.

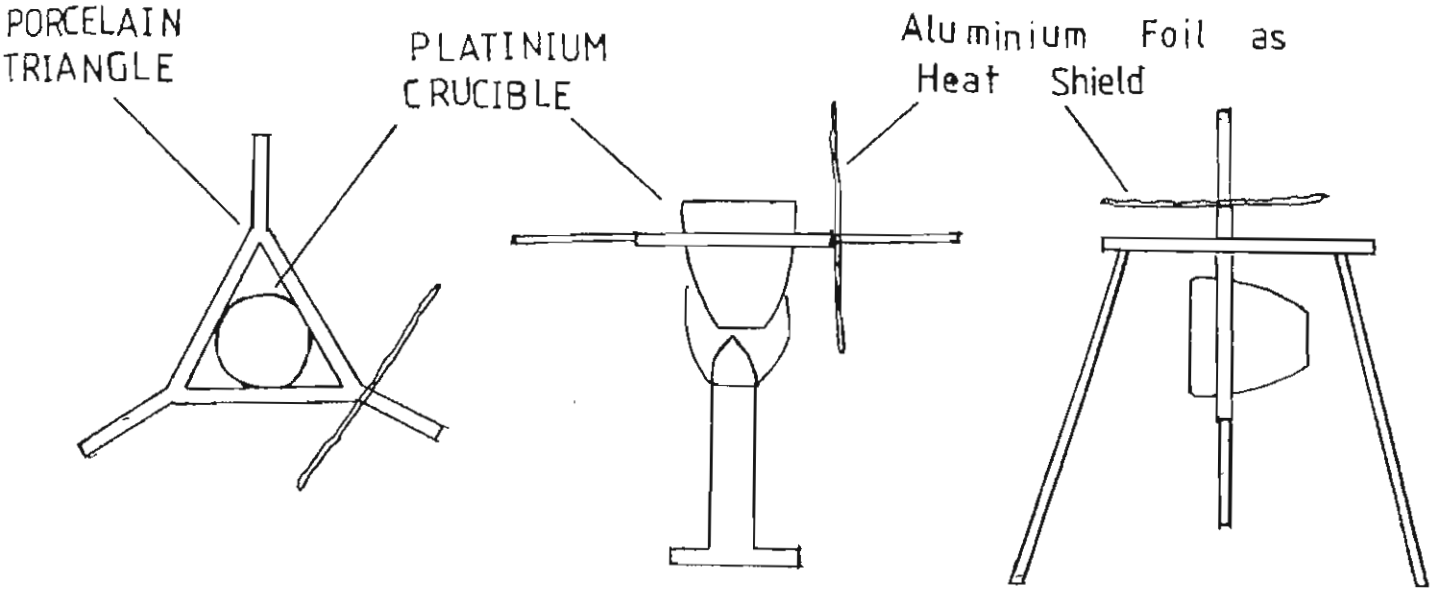
The crucible was removed from the flame and allowed to cool on its side. The solidified melt,which could be largely removed by gently squeezing the sides of the crucible, was then transferred to a 25 ml beaker. A sulphuric acid solution of 4 ml concentrated sulphuric acid and 8 ml of distilled water was used to rinse the crucible and the washings added to the melt. The beaker was gently heated on a hot-plate until the melt disappeared completely and, upon cooling, the solution was transferred to a 50 ml volumetric flask and diluted to the mark with distilled water.

Points of Note on Fusion Method

1. Any attempt to fuse the ilmenite with potassium hydrogen sulphate without first expelling the water would inevitably result in frothing, effervescence and subsequent loss of sample.

FIG. 3

SKETCH DIAGRAMS SHOWING STEPS IN FUSION METHOD



a. Crucible sits tightly in porcelain triangle

b. Regulated heating to induce fusion

c. Crucible with melt cooling on its side

2. The melt formed from fusion with three grams of potassium hydrogen sulphate only without the benefit of the second fusion, was difficult to redissolve in acid solution and deposition of a white precipitate often occurred. A probable explanation was that the white precipitate was insoluble basic sulphate (titanyl sulphate - $TiOSO_4$) which arose through decomposition of titanium sulphate at high temperatures (Sear and Quill,1925). The second fusion served the purpose of converting the insoluble basic sulphate to the soluble sulphate form.

Invariably however some of the solutions so prepared carried small amounts of a white precipitate that quickly settled to the bottom of the flask. The precipitate as examined by x-ray fluorescence scan was found to contain mainly titanium probably in the hydrolysed form [$Ti(OH)_4$] but carried negligible amounts of the elements under analysis.

Interference Study and Compensation Measures

The sample solution prepared in this way contained, apart from titanium and iron, (which are the main cationic species from ilmenite), large amounts of potassium hydrogen sulphate and sulphuric acid. The possible interference effects of these on the AAS determination of the minor elements were therefore investigated. The procedures of O'Shaughnessy (1978) were followed and this involved adding to a number of standard solutions of a selected element different combinations of potassium hydrogen sulphate, (added as a melt formed from fusing 4g of potassium hydrogen sulphate for 15 to 20 minutes), sulphuric acid, titanium and iron, (equivalent to ·25g ilmenite). Their AA absorbances were measured and compared.

These results are summarised in Table 2:4 (a - f). It is evident from these tables that for all the elements (V, Cr, Mn, Ni, Cu, Mg) tested, interference effects from potassium hydrogen sulphate, sulphuric acid, titanium and iron do arise.

Rather than compensating for these effects by adding the appropriate amounts of potassium hydrogen sulphate, sulphuric acid, titanium and iron to the calibration standard solutions, it is simplier and more convenient to use a 'correction factor' derived from the tables, and calibration solutions prepared to the same acidity as the sample solutions. Prior to the determination of the concentration of an element in the sample solution from the calibration graph, its absorbance (peak height) was multiplied by the 'correction factor' for that element. In Table 2:4a for example the combined effect of $KHSO_4$, Ti and Fe depressed the absorbance (peak height) from 83 mm to 63 mm (after allowance for the blank). Since most of the sample solutions fell within the linear portion of the calibration graph, it was possible to make suitable adjustment for the interference effect by raising the absorbances recorded for the sample solutions by a factor of 83/63.

Although the correction factor could vary slightly for solutions with different concentrations of the element, the standard solution chosen for deriving the correction factor was such that it represented the average concentration for the element in ilmenite solutions. Hence the correction factors required for other concentrations would not deviate significantly from it.

The operating conditions for AA5 Analysis were essentially the same as in Table 2:3 for the magnetite

analysis except that sensitivity was sometimes varied for some elements by using different wavelengths to allow for differing concentrations.

Calculation of the minor element concentrations in the ilmenite sample from the sample solution concentration readings is similar to that given under magnetite analysis.

TABLE 2 : 4

'CORRECTION FACTORS' FOR ANALYSIS OF ILMENITE

Vanadium a

	Absorbance (Peak Height mm.)
5 ppm V	68
5 ppm V + H_2SO_4 (4 ml conc.H_2SO_4/50 ml soln)	83
5 ppm V + H_2SO_4 + $KHSO_4$	87
5 ppm V + H_2SO_4 + $KHSO_4$ + Fe@ + Ti@	67
5 ppm V + H_2SO_4 + Fe + Ti	73
Blank (H_2SO_4 + Fe + Ti)	4
Correction factor	$^{83}/_{63}$ = 1·317

@ equivalent to ·25g ilmenite ($FeTiO_3$)/50 ml soln.

Chromium b

	Absorbance (Peak height mm.)
4 ppm Cr	48
4 ppm Cr + H_2SO_4	53
4 ppm Cr + H_2SO_4 + $KHSO_4$	52·5
4 ppm Cr + H_2SO_4 + $KHSO_4$ + Fe + Ti	52
4 ppm Cr + H_2SO_4 + Fe + Ti	56·5
Blank (H_2SO_4 + Fe + Ti)	4
Correction factor	$^{53}/_{48}$ = 1·104

Manganese c

	Absorbance (Peak height mm.)
20 ppm Mn	38·5
20 ppm Mn + H_2SO_4	39
20 ppm Mn + H_2SO_4 + $KHSO_4$	36
20 ppm Mn + H_2SO_4 + $KHSO_4$ + Fe + Ti	51·5
20 ppm Mn + H_2SO_4 + Fe + Ti	47
Blank (H_2SO_4 + Fe + Ti)	13
Correction factor	$^{39}/_{38.5}$ = 1·01

Nickel d

	Absorbance (Peak height mm.)
10 ppm Ni	85·5
10 ppm Ni + H_2SO_4	85·5
10 ppm Ni + H_2SO_4 + $KHSO_4$	82·5
10 ppm Ni + H_2SO_4 + $KHSO_4$ + Fe + Ti	83·0
10 ppm Ni + H_2SO_4 + Fe + Ti	85·0
Blank (H_2SO_4 + Fe + Ti)	12
Correction factor	$85·5/71$ = 1·204

Copper e

	Absorbance (Peak height mm.)
1 ppm Cu	52·0
1 ppm Cu + H_2SO_4	55·0
1 ppm Cu + H_2SO_4 + $KHSO_4$	55·5
1 ppm Cu + H_2SO_4 + $KHSO_4$ + Fe + Ti	57·5
1 ppm Cu + H_2SO_4 + Fe + Ti	56·5
Blank (H_2SO_4 + Fe + Ti)	9
Correction factor	$55/48·5$ = 1·134

Magnesium f

	Absorbance (Peak height mm.)
20 ppm Mg	62·0
20 ppm Mg + H_2SO_4	58·5
20 ppm Mg + H_2SO_4 + $KHSO_4$	57·0
20 ppm Mg + H_2SO_4 + $KHSO_4$ + Fe + Ti	56·5
20 ppm Mg + H_2SO_4 + Fe + Ti	58·5
Blank (H_2SO_4 + Fe + Ti)	6
Correction factor	$58·5/50·5$ = 1·158

CHAPTER III

SOME MINERALOGICAL CONSIDERATIONS

This section surveys briefly those aspects of mineralogy which are relevant to the development of the work described in this thesis. These comprise the following:

1. Persistence Characteristics of Minerals

   This is important since the already fine-grained minerals carried down-river and accumulating in the beachsands are subject to heavy abrasion as well as chemical degradation.

2. The Characteristic Mineral Association in Metamorphic Rocks

   In Westland a high proportion of the beachsand detrital minerals come from the schists in which mineral assemblages will be dependent upon both the composition of the original sediments and on the grade of the metamorphism.

3. Factors Controlling Isomorphous Replacement Within Minerals

   This is particularly relevant to the Chapter on minor elemental composition in magnetite and ilmenite, but does of course underly the general property of minerals in showing some variability in composition.

Persistence Characteristics

Persistence characteristics of heavy detrital minerals in the Westland area have been summarised by Bradley et.al. (1979), (see Appendix 4). It is obvious

that only the persistent minerals can be expected to accumulate on the beaches. Particular importance is attached to the accumulation of magnetite and ilmenite within the beachsands, as dealt with in Chapters IV and V. It is important to note that both these minerals are in the high persistent class and within the time span involved in beachsand accumulation they can be regarded as equally persistent. Where magnetite is derived from ultramafic sources it is chromium-rich, and just as chromite itself is of high persistence, so also there is no evidence of any progressive loss of chromium from chromium-rich magnetite. Garnet, orthopyroxene, tremolite are also in the persistent class, so that their presence or absence within the beachsands can be a significant factor in relation to sources of supply.

Mineral Associations in Metamorphic Rocks

During regional metamorphism, taking place over a long interval, a state of equilibrium is generally attained. Under such a state according to the mineralogical application of the Phase Rule, "the number of minerals capable of existing together as separate phases in a system is equal to the number of components" (Mason,1966). This is on the assumption that the conditions under which equilibrium is attained are specified by fixing the two variables, temperature and pressure. Thus, if there are eight components such as SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, FeO, Fe_2O_3, eight phases would thereotically be expected in proportions depending on the original composition. In practice there can be complications arising from isomorphous replacement. For example, Fe^{2+} and Mg^{2+} may act as a single component and

mask each other. Moreover, there is also the possibility that minor components such as TiO_2 and MnO may or may not produce new distinct phases.

In general the number of minerals that normally form as major constituents would be fewer than the number of components (Mason, 1966 pp261). Nevertheless, the types of mineral that develop would depend on the prevailing physical conditions of temperature and pressure. If rocks of known bulk composition are subjected to progressive metamorphism with change to new P-T conditions, mineral transformations will occur. An example of a mineral transformation leading to the conversion of chlorite to epidote would be :

3 chlorite + 10 calcite = 2 epidote + 3 actinolite + 8 CO_2 + 10 H_2O.

(Cooper, 1971).

Some minerals remain stable over only a limited range of (P-T) conditions while others are stable over a wide range.

Geological mapping of the Alpine Schist has been carried out mainly in terms of metamorphic grades based on significant mineral occurences. The Chlorite 1-4, biotite, garnet and oligoclase zones can all be clearly differentiated. This classification gains an added importance because the compositions of the parent sediments were rather uniform over wide areas (Reed, 1957; Mason,1962).

The facies classification provides an additional advantage in allowing for differences in regional composition of the parent rocks before metamorphism. It is reflected not so much in the types of minerals that develop but rather

in the proportions in which they are present.

In the present work this is particularly important in considering the mineralogy of the schists in the Jackson Bay-Haast region which have been derived from more basic parent rocks than have the Alpine schists north of about the Haast River. The consequences of this are discussed in Chapter IV.

Isomorphous Replacement

Since minerals usually crystallise slowly under conditions that provide access of a wide variety of ions, isomorphous replacement is a common feature. In its simpliest terms the process involves the substitution of ionic components in the characteristic crystalline lattice of a mineral with ions of similar size. The size requirement is important because the substituting ion must be accommodated in the crystal lattice without so much distortion as might lead to the appearance of a new phase. The radii of the substituting and substituted ion should not usually differ by more than 10-15%. Thus Fe^{2+}(0·75Å) and and Mg^{2+}(0·65Å) are interchangeable in 'ferromagnesium' minerals. Likewise ions such as Ni^{2+}(0·70Å), Cu^{2+}(0·73Å), Mn^{2+}(0·80Å) can replace Fe^{2+}, and the trivalent ions V^{3+}(0·66Å), Cr^{3+}(0·64Å), Fe^{3+}(0·60Å), Al^{3+}(0·53Å) can substitute for each other. It is thus to be expected that magnetite, Fe_3O_4, with its spinel $M^{II}M^{III}O$ structure, would carry the ferride ions with the +2,+3 oxidation states.

The charge on a substituting ion is not particularly important (perhaps a change of ±1) provided that charge balance is maintained within the lattice as a whole. Thus tetravalent ions like Ti^{4+}(0·61Å) and Si^{4+}(0·42Å) also

replace Fe^{3+} in the magnetite structure and are probably accompanied by the substitution of Fe^{3+} with divalent cations to restore charge balance. In the plagioclase series Ca^{2+}(0·99Å) can replace Na^{+}(0·98Å) in passing from albite ($NaAlSi_3O_8$) to anorthite ($CaAl_2Si_4O_8$) and electrical neutrality is maintained by the simultaneous substitution of Al^{3+} for Si^{4+}.

Apart from the influence of size and charge, some authors have cited "electronegatives" of cations as an important factor in controlling isomorphous replacement. Ringwood (1955) expresses the electronegativity factor in the form of a rule; "When diadochy in a crystal is possible between two elements possessing appreciably different electronegativities, the element with the lower electronegativity will be preferentially incorporated because it forms more ionic bond than the others". In chemical terms this perhaps means that a cation can be expected to substitute the more readily into an ionic oxide lattice if it is well suited to the maintenance of ionic (rather than covalent) bonding interactions.

It must also be remarked that the type of structure possessed by a mineral, including its tolerance towards lattice defect and local deformations, must also influence these substitutions. Structures such as those of the spinel and apatite are well known for extensive ion substitution, whereas others such as quartz show very little. In connection with the present work it seems that there are characteristic differences in substitution as between magnetite and ilmenite which are not entirely connected with cationic size and charge.

Attention is often directed towards the somewhat greater substitution at high temperature than at low temperature. For example, Lister (1966) found that the percentage of minor elements in magnetite increases as the temperature of formation of the magnetite increases. This effect probably arises from a greater tolerance of lattice strain and defect at higher temperature as a result of increased thermal vibrations.

Apart from the temperature effect, it must also be mentioned that the degree of substitution also depends on the concentration of suitable cations present in the medium. For this reason early stage minerals may carry more substituting ions than minerals formed at a later stage.

CHAPTER IV

BEACHSAND MAGNETITE IN THE JACKSON BAY-HAAST AREA

In the Jackson Bay-Haast area there is an isolated 50 km segment of continuous beach between Jackson Bay itself in the south-west and Tauperikaka Point to the north-east. The blacksand on this stretch of beach differs from that on the beaches to the north in containing a preponderance of magnetite rather than ilmenite over its length (see Table 4:1 and Fig. 4). In each of two reports on ilmenite resources there is mention,without comments, that sand from Okuru aerodrome (Nicholson et.al., 1958) and from a roadside drill-hole near Carters Mill (Carpentaria Exploration Company Report 217, 1971) were rich in magnetite rather than ilmenite. This section concerns the source of the beachsand magnetite.

I GENERAL FEATURES OF THE REGION

The coastal area between the beaches and the Alpine Fault comprises an unusually low-lying strip 5-8 km in width, with the schist mountains immediately behind the Fault (Wellman and Willet, 1942). The Arawata, Waiatoto, Turnbull, Okuru and Haast Rivers which flow across the coastal strip drain some 3000 km^2 of schist of grades varying in the main from chlorite IV to garnet-oligoclase Several small hummocks of granite and Palaeozoic metasediments protrude through the swampy terrain. There are also two high-standing (Ca.600 m) granite domes - Mt McLean in the south and Mosquito Hill north of the Haast River. The aspect strongly suggests that the strip once carried a piedmont glacier.

TABLE 4 : 1

MAGNETITE AND ILMENITE CONTENTS OF BEACHSANDS[a]

Locality	% Heavies in 3ϕ Cut	Magnetite % of Heavies	Ilmenite % of Heavies	I:M Ratio
Neils Beach[b]	8	4.4	1.9	0.43
1 km north Arawata	20.8	16.4	5.1	0.31
3 km north Waiatoto	99	93	2.6	0.027
5 km north Waiatoto[c]	31.5	74	5.8	0.078
9 km north Waiatoto[d]	65.5	84	1.9	0.023
1.5 km south Haast[e]	12.0	7	8.9	1.27
3 km north Haast[f]	96.9	30	42	1.43
2 km north Waita	47.1	8.2	37	4.5[g]

[a] The percentages refer to 3ϕ sieve fractions from samples collected close to the high-tide mark.

[b] 1.5 km west of Arawata mouth.

[c] At Carters Mill.

[d] At Mussel Point.

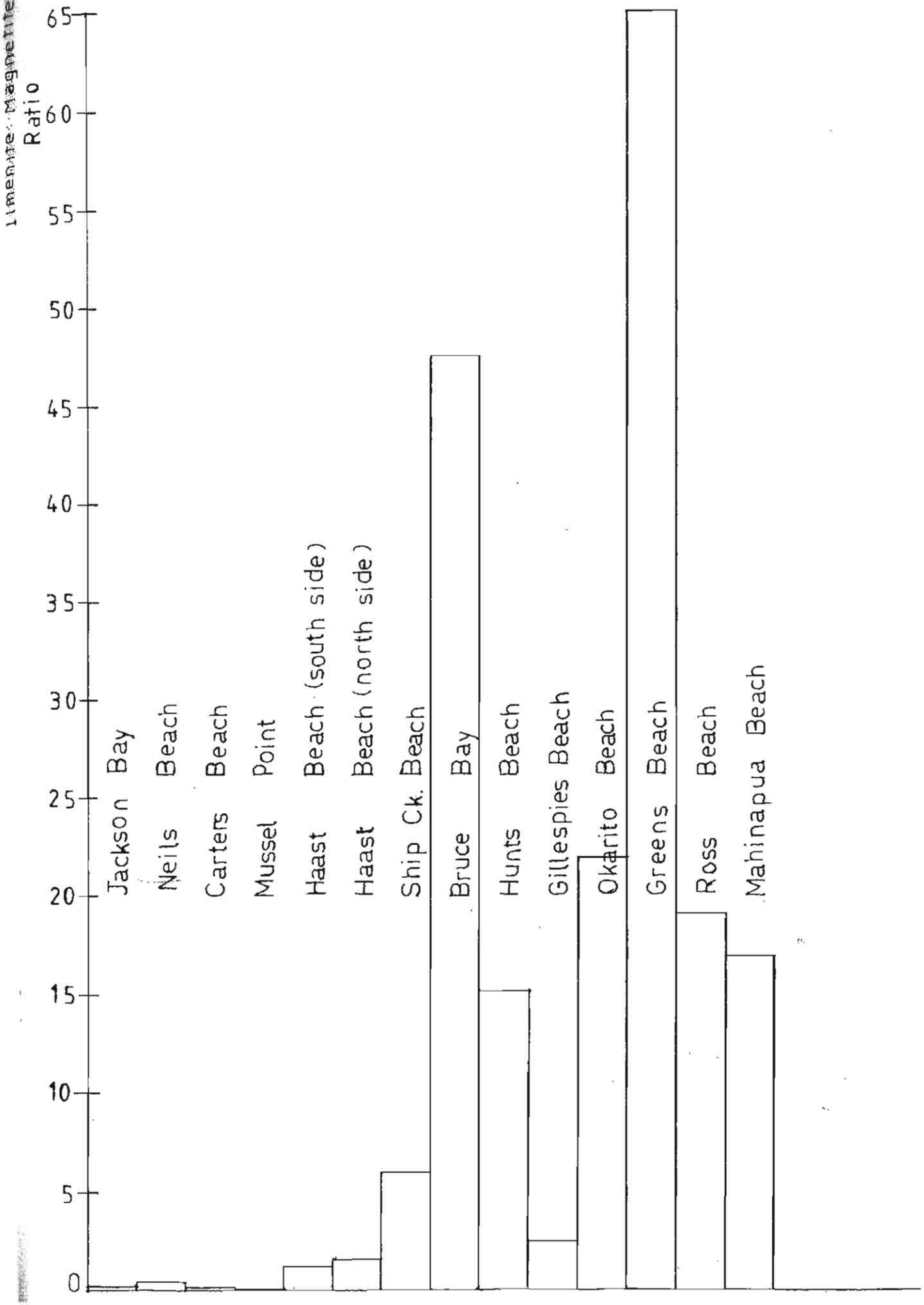
[e] At Haast township.

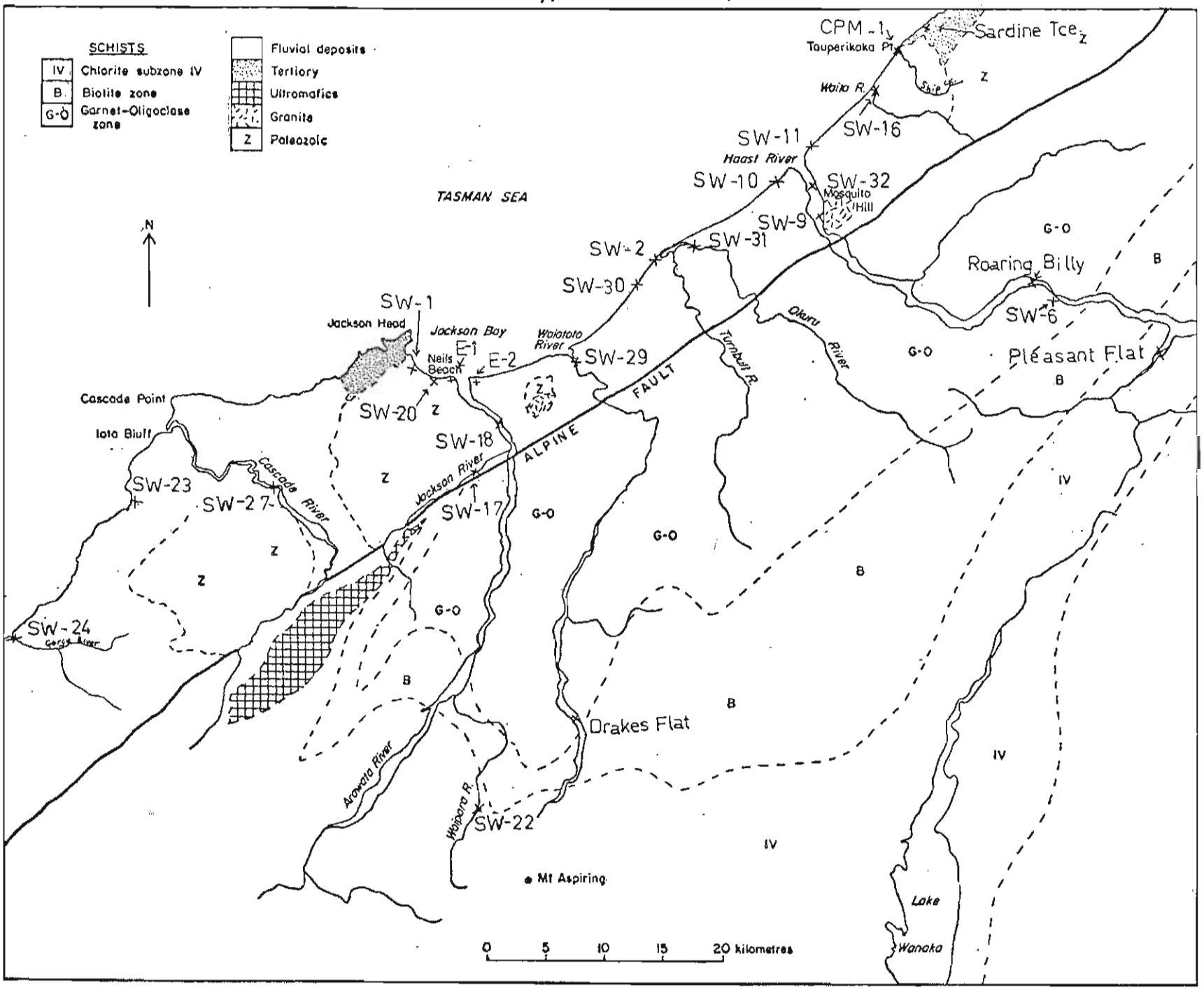
[f] The concentration of blacksand in this particular sample was unusually high.

[g] A sample from Tauperikaka Point, alongside Ship Creek, gave a ratio 6.0.

Fig. 4

Ilmenite : Magnetite Ratios of Westland Beachsands in South-North Direction (3 ϕ).




SCHISTS
IV Chlorite subzone IV
B Biotite zone
G-O Garnet-Oligoclase zone
Fluvial deposits
Tertiory
Ultramafics
Granite
Z Paleozoic
TASMAN SEA
N
CPM-1
Tauperikaka Pt
Sardine Tce
Waiia R.
SW-16
SW-11
Haast River
SW-10
SW-32
Mosquito Hill
SW-9
SW-31
SW-2
SW-30
Roaring Billy
SW-6
Pleasant Flat
SW-1
Jackson Head
Jackson Bay
Neils Beach
E-1
E-2
Waiatoto River
SW-29
Okuru River
Turnbull R.
FAULT
ALPINE
Cascade Point
Iata Bluff
SW-20
SW-18
SW-23
SW-27
Cascade River
Jackson River
SW-17
SW-24
Gorge River
Drakes Flat
Arawata River
Waipara R.
SW-22
Mt Aspiring
Lake Wanaka
0 5 10 15 20 kilometres

To the south-east along the Alpine Fault lie areas of ultramafic rock from which the Jackson River, flowing north-east along the fault, provides drainage directly into the lower Arawata River (Mutch and McKellar, 1964). The southern flank of the low-lying area between the Jackson River and Jackson Bay is bounded by a block of Palaeozoic metasediments. On the northern flank the area is bounded chiefly by a similar Palaeozoic block with fringing Okarito Formation moraine. Here the drainage is by two small streams, the Waita River and Ship Creek entering the sea at the northern end of the low-lying coastal region (see Fig.5).

II SOURCE OF MAGNETITE

Evidence is sought as to whether the beachsand magnetite may have been derived from the ultramafic source, from the schists,or from both. The Tuhua Granites of North Central Westland provide a richer source of magnetite than do the schists in that area (Bradley et.al., 1979). However, in the Haast region, the small area of granite (Ca.7 km^2), and in part its low relief, must exclude any significant magnetite contribution. The Palaeozoic sediments provide little drainage into the sea and in any case are low in detrital heavy minerals. As regards the possibility of coastal transport of beachsand into the area, longshore drift is from the south; but at the present time there can be little, if any, progressive transport of sand along the rocky coast between Cascade Point and Jackson Head, although an isolated pocket of sparse sand with ultramafic magnetite containing 5·6% chromium was found.

Turner (1933) has reported the rather common occurrence of (accessory) magnetite within the schists of this area. This

is hardly reflected in the composition of the fine (3ϕ and 4ϕ) detrital sediments, for which the Waipara, Waiatoto and Okuru Rivers all give ilmenite:magnetite ratios of 1·4-1·6, and Haast, 3·7 (see Table 5:2). However, large amounts of coaser magnetite (0·5-1 mm) can readily be collected from the river gravels with a hand-magnet (e.g. Waiatoto River at Drakes Flat, Lower Okuru River, Haast River at Pleasant Flat). Moreover, the ilmenite:magnetite ratio falls abruptly in the beach-sand immediately north-east of the Waiatoto Mouth (Table 4:1). There is thus direct evidence that the Waiatoto River makes a major contribution to the high concentrations of beachsand magnetite.

Chromium Content in Magnetite as a Chemical Indicator

The picture is confirmed by the pattern of the chromium contents of magnetite samples over the region. Ultramafic rock is characteristically high in chromium, largely present chromium-rich magnetite or as chromite itself. The chromium-rich magnetite sand from the Jackson River ("bulk composition", 9200 ppm) reaches the beach by way of the Arawata mouth. A great part of the magnetite derived from the schists has a typical chromium content 150-500 ppm (see Table 7:1), and because complications are relatively minor, a broad picture of the dispersal of the ultramafic magnetite and its dilution by schists magnetite can be deduced from the pattern of the chromium contents of samples taken over the area. Results of analyses are plotted in Fig. 6. Along the beaches continuing attrition of coarser low-chromium magnetite is to be expected, and with fresh exposures after storm conditions, there can be

variations of up to 10% in the chromium values at a particular site. It may be noted also, that the high value of 1700 for a sample from the lower Okuru River is probably attributable to ultramafic pods within the catchment of this river; one such pod has been examined by Cooper (1976).

Although the coastal transport of the bulk of the sediment from the Arawata River is to the north-east, a magnetite sample collected 0·5 km to the west of the river mouth gave a chromium value of 6290 ppm, fortuitously somewhat higher than values for magnetite collected from the lower river (5700), but clearly indicated derivation from the river. For magnetite from Neils Beach, 1 km further to the west of the river mouth, and almost at the extreme south-western end of the sandy beaches, the value was 3580. Magnetite from the sparse fine sediments 4 km further west against the headland at Jackson Bay settlement gave a similar chromium figure, 3940 ppm.

With transport of sediments mainly to the north-east, the nature of the beachsand on that side of the river mouth could be expected to show a quicker response to river conditions. It is therefore of interest that the chromium content (5350) of a 3ϕ beachsand magnetite sample collected Ca. 0·7 km to the north-east of the river -mouth was almost the same as that of the magnetite from the lower river. Chromium values for 3ϕ magnetite decrease progressively along this beach, to 1400 at Carters Mill (between Waiatoto and Turnbull Rivers) and to 870 at the southern end of the Turnbull-Okuru Lagoon. The decrease is due to admixture with the Waiatoto River magnetite (770 for 3ϕ material) and to continuing coastal attrition of coarse

FIG. 6 Jackson Bay – Haast Area : Chromium Values of Magnetites (ppm).

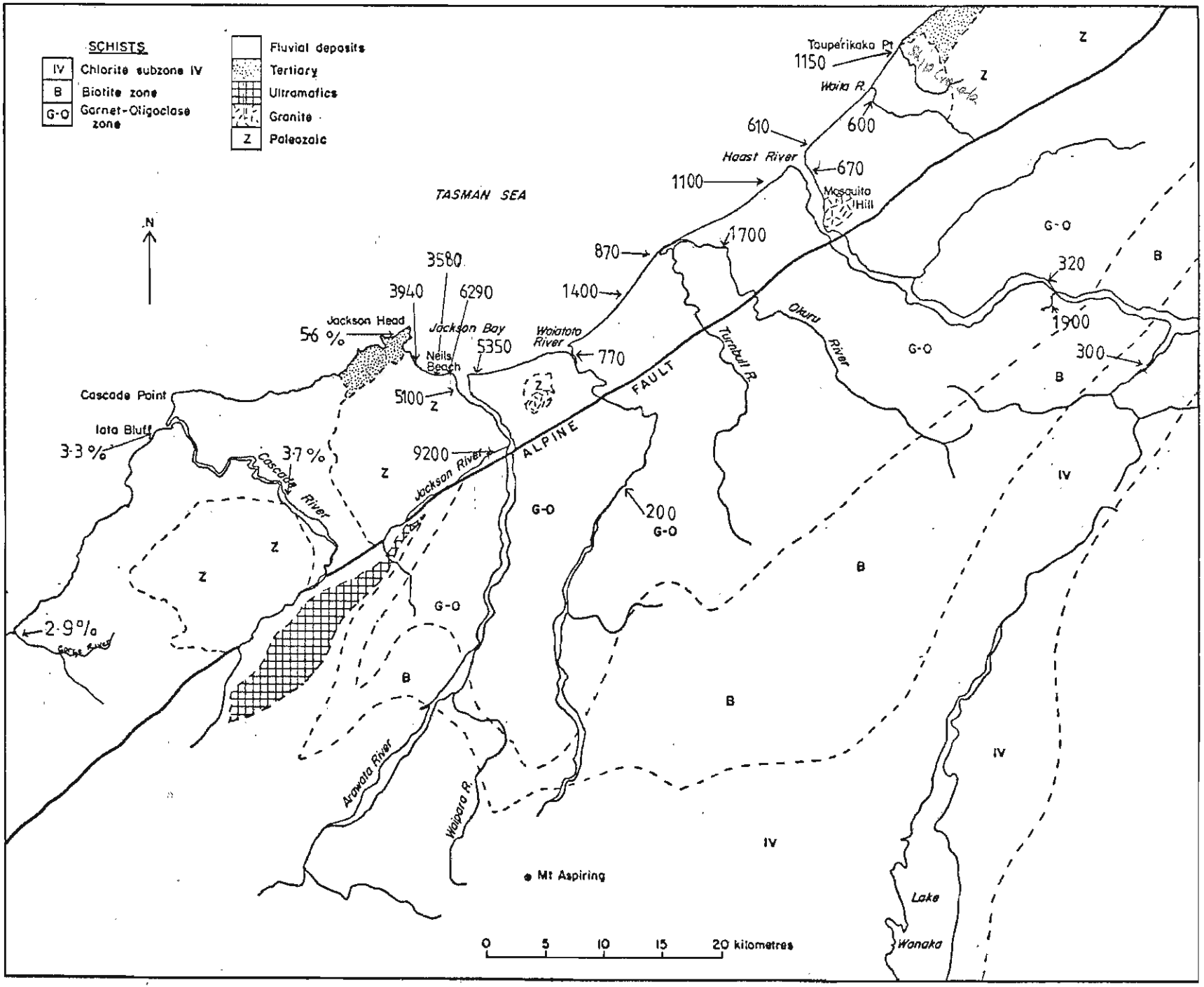


TABLE 4 : 2

MINOR ELEMENT CONTENTS IN MAGNETITE[a] FROM RIVER SEDIMENTS AND BEACHSANDS OF JACKSON BAY-HAAST AREA (ppm)

	Locality	Code	Ti	V	Cr	Mn	Ni	Cu	Zn	Mg
River Sediments	Arawata R.	SW 18	2,410	840	5,140	1,070	2,350	66	183	25,600
	Jackson R.	SW 17	1,710	558	9,180	1,630	2,690	90	222	60,600
	Waiatoto R.	SW 29	1,320	1,320	770	361	289	39	125	1,040
	Drakes Flat[b]	-	1,340	1,310	198	593	128	13	60	466
	Okuru R.	SW 31	25,000	1,210	1,700	2,700	560	82	260	-
	Haast R.	SW 32	11,840	1,510	670	1,240	572	149	307	7,510
	Pleasant Flat[c]	-	4,000	1,350	299	593	159	20	97	1,080
	Roaring Billy[d]	-	2,400	1,440	322	541	162	12	74	400
	Waita R.	SW 16	5,900	1,750	600	620	270	33	170	-
Beachsands	Jackson Bay	SW 1	2,110	1,270	3,940	751	264	20	141	3,100
	Neils B.	SW 20	2,330	1,190	3,580	736	433	27	161	6,940
	.5 km S-W Arawata Rm.	E 1	1,970	1,340	6,290	994	502	27	130	9,140
	1 km N-E Arawata Rm.	E2	1,590	1,230	5,350	879	400	24	121	6,610
	Carters Mill B.	SW 30	1,750	1,220	1,380	587	119	14	97	-
	Mussel Point B.	SW 2	1,730	1,170	866	507	99	14	126	574
	Haast Township B.	SW 10	1,640	1,190	1,100	521	137	18	116	522
	3 km North of Haast Rm.	SW 11	3,270	1,350	613	707	227	16	77	300
	Ship Creek B.	CPM 1	14,790	1,550	1,150	1,240	420	67	647	6,070

[a] Magnetite (3ϕ and less) extracted from bulk samples or collected as 'concentrates'.

[b] A coarse size magnetite sample from Upper Waiatoto.

[c,d] Field concentrated Magnetite from the Upper Haast.

grained low-chromium schists magnetite be Between the Okuru and Haast Rivers the higher chromium content of magnetite from the Okuru (1700) produces a small increase in the beachsand values. North of the Haast River-mouth the overwhelming effect of the Haast River sediments reduces the chromium content sharply.

The beachsand concentration of magnetite (Table 4:1) also becomes lower in the vicinity of the Haast River-mouth, and for practical purposes the Haast may be taken as the northern boundary of the magnetite-rich zone. Sediments from the small Waita River draining Ca.60 km^2 schist and 15 km^2 Okarito Formation, and entering the sea 11 km north of the Haast gave ilmenite:magnetite ratio of 8·8. But the chromium content of its magnetite (600 is similar to the value from lower Haast. A beachsand ratio from a sample between the Waita River and Ship Creek was 4·3:1, indicating a considerable influence of these neighbouring (even though small) rivers on the beachsand composition. It is of interest that a magnetite sample from the beach at Ship Creek gave a chromium figure of 1150. This indicates accession, by longshore drift, of some chromium-rich magnetite from the beaches to the south-west, notably from the Arawata-Waiatoto area.

For completness, concentration of other minor elements in the magnetite samples from this region are given in Table 4:2.

Mineral Assemblage in Heavy Detrital Concentrates

Beyond magnetite and ilmenite, Table 4:3 lists all detrital heavy minerals in the river sediments and beachsands. The beachsand accumulations are consistent with the

TABLE 4 : 3

Composition of Magnetic Fractions[a,b]

Source and Sample no.	Magnetite	0.2 Amp	0.35 Amp	0.45 Amp	0.75 Amp	1.2 Amp	Non-magnetic
Cascade R. SW28	MM	C,An,G,I E*,H*,B*	EE,H(g/b) I,B,Mu	EE,HH(g/b)	EE,OpOp, ZoZo,MuMu,H*	Tr,Zo,S,Op	Z,S,Ap R*,P*
Jackson R. SW17	MM	H(g/b)I,E G,B,R	EE,H(g/b) I,B,Mu,Tr	EE(alt),L MuMu,H,B,Tr	Mu,L,S, E,An*	SS,L,Mu R*	Mu,Z L,S,P*
Waipara R. SW22	MM	CC,H,B,I	HH,C,I,B	MuMu,EE H*,Tr*	MuMu,E,Tr	SS,Ap,Mu	ApAp,Z
Arawata R. SW18	MM	HH,I,EE B,G	EE,L,HH BB,MuMu,G*	EE,LL, MuMu,I,H	EE(incl),MuMu II,L,T,Tr*	SS,L,Mu E(alt),R*	ApAp,Z Mu,L*,R*
Waiatoto R. SW29	MM	HH,II,E,G*	HH,EE, II,L,B	EE(alt),MuMu LL,I,B(alt)	Mu(alt),L, S(alt)I,EE(alt)	SS(alt),L MuMu(alt),R*	SS(alt),Ap LL,Mu
Haast R. SW9	MM	I,H,GG C,E,B*	EE,H,P, T*,L*,B*,Ca	EE,H,P, T*,R*,L*	SS,EE,LL MuMu,P*,R*,T*	SS,L,Z*,R* F*,Mu*,T*,P*	Z,Ap,LL S,P*,R*
Neils Beach SW20	MM	I,B,G,C	EE,GG,BB, I,H,C*	EE,BB,Tr*	EE,B,Tr*	SS,E,L R*	SS,Z,Ap L*,R*
Arawata Beach E2	MM	HH,I,G,C	EE,I,C,G H,B	EE,Mu,B	EE,Op,Tr*	SS,Ap,R*	ApAp,S,Z
Carters Mill SW30	MM	II,GG,B	EE,G,I,B, H,	EE,B,Tr*	EE,B,P*	S,E,Z,P*,R*	SS,Z,Ap,R*, Hy*
Haast Beach (south)SW10	MM	II,G,E,B,H	G,E,II,HH, B,	EE,L,H,B R*,T*	E,L,MuMu T*,R*,An*	SS,E,L,Mu,	ZZ,S,Ap,L, Mu
Haast Beach (north)SW11	MM	II,G,C*	GG,II,E	EE,B,G,L, Mu,P,T*	EE,B,L, Mu	S,E,L,Mu,R*	ZZ,S,Ap*, Hy*,R*,Gold*
Tauperikaka Pt. CPM 1	MM	II,G,E,H B*Mu(alt)	EE,GG,LL I,Mu,H,R	EE,LL,GG R*,An*	LL,S,E Mu,	LL,S(alt) MuMu,E	L,Z,S ApAp,Mu

[a]Samples were handled and mineral identifications carried out as previously described (Bradley, 1977; Bradley et al. 1979).

[b]The lettering indicates the abundance of each element within individual magnetic cuts:

XX = main constituent, >40%; X = 15 - 40%; XX = 5 - 15%; X = 1 - 5%; X* = < 1%.

(incl) = inclusions present. (alt) = altered. H(g/b) = green and brown hornblende, where the typical green mineral from the schists is mixed with a brown ultramafic component.

Ap = Apatite; An = Anthophylite; B = Biotite; C = Chlorite; Ca = Carbonate; E = Epidote; G = Garnet; H = Hornblende; Hy = Hyancinth zircon; I = Ilmenite; L = Leucoxene; M = Magnetite; Mu = Muscovite; Op = Orthopyroxene; P = Pyrite; R = Rutile; S = Sphene; T = Tourmaline; Tr = Tremolite-actinolite; Z = Zircon Zo = Zoisite.

composition of the riversands and the north-eastwards coastal transport. River sediments from the Biotite and Garnet-oligoclase zones are notably high in hornblende (as for the Waiatoto and Okuru Rivers), but low in biotite and garnet. Abundant chlorite from the chlorite iv zone (Waipara River) rapidly disappears through low persistence (Bradley et.al., 1977) (see Appendix 4) and appears in only the most recent beachsands, as in the vicinity of the Arawata and Haast Rivers. Hornblende passes onto the beaches but does not accumulate proportionately, through its only moderate persistence.

The particularly high magnetite concentrations north of the Waiatoto River are due not only to the rich supply from that river (especially in relation to the low ilmenite and garnet) but also to the gradual disappearance of hornblende and to the effective wave-sorting of magnetite (d=5·2) from epidote (d=3·2-3·4) of similar grain size.

The Cascade River, like the Jackson, carries anthophyllite and tremolite. There is sparse anthophyllite in the beachsand at Haast and at Ship Creek. A connection with the presence of the mineral in the Jackson River sediment is possible but not established.

III COMPARISON WITH DETRITAL MINERAL ASSEMBLAGES FROM SCHISTS TO THE NORTH

The equilibrium mineral assemblage in schist is determined by conditions of metamorphism, with the proportions dependent upon the composition of the parent material as required by the application of the Phase Rule to schist mineralogy, as already discussed in Chapter III. Apart from the predominance of magnetite over ilmenite, the heavy

mineral assemblage in rivers south of the Haast differs from that typical of the more northern rivers draining the same grades of schist in containing a higher proportion of hornblende, and possibly epidote, but less ilmenite, garnet and biotite (Table 4:4).

In North Westland the schists are of quite uniform composition corresponding to the Torlesse series, but are occassionally intersected by metavolcanic bands (Mason and Taylor, 1955). Little or no hornblende developes in the metasediments for which CaO averages only 2·0%, and iron (as FeO) 4·1%, but hornblende is a major component of the metavolcanics. It can be seen from Table (8:3) that the heavy mineral concentrates from the Central Westland Rivers, particularly those between Karangurua and Wanganui, contain only small amounts of hornblende, but for the South Westland rivers (Arawata-Paringa), the presence of hornblende is more conspicuous, and, as expected, the content of hornblende in sediments from the Jackson, Cascade and Gorge Rivers, is very small.

In the Jackson Bay-Haast area, it can be expected that the contribution of the greenschists (Cooper and Lovering, 1970; Cooper, 1972) to the high detrital hornblende content, but this does not explain the low proportions of ilmenite, biotite and garnet in the total sediments. Although whole rock analyses on the schists in this area do not seem to be available, the high proportions of hornblende and epidote in the detrital mineral assemblage point to a generally higher calcium, and probably iron, content than in the north. Besides calcium, formation of epidote also requires aluminium and iron (II) and hornblende requires aluminium and iron (III). Plagioclase formation will continue the aluminium demand.

TABLE 4 : 4

PERCENTAGES OF COMPONENTS IN HEAVY MINERAL CONCENTRATES[a]

River	Ilmenite	Biotite	Hornblende	Epidote	Garnet
Griffin[b]	9	10	-	26.5	19
Poerua[c]	15	9	5	24	5
Karangarua[d]	22	12	9.5	25	11
Haast	7	3	14	28	3
Waitoto[e]	3	2	26	33	0.1
Okuru[e]	2	2.7	26	35	0.1
Waipara[f]	1.5	2	20	20	-

[a]Comprising 3ϕ + 4ϕ sieve fractions.

[b]Tributary of the Taramakau draining only Biotite and Garnet-oligoclase zones.

[c]Central Westland, draining Biotite and Garnet-oligoclase zones.

[d]South-Central Westland, draining Chlorite III, IV, Biotite and Garnet-oligoclase zones.

[e]Drains Biotite and Garnet-oligoclase zones. The close similarity in the sediment compositions from the neighbouring Okuru and Waiatoto Rivers draining the same schist zones is evident.

[f]Arawata tributary, draining Chlorite IV, with greenschist bands.

It is suggested that uptake of aluminium in the preferential formation of these calcium-rich phases is the main factor prohibiting the formation of garnet. Because titanium released from some of the early formed sphene (Force, 1971) substitutes readily into hornblende, formation of ilmenite is also reduced. Considerable local variations in the magnetite content of the rocks are probable because its formation must depend upon the balance between the iron content and the demand for iron in the formation of epidote, hornblende and biotite.

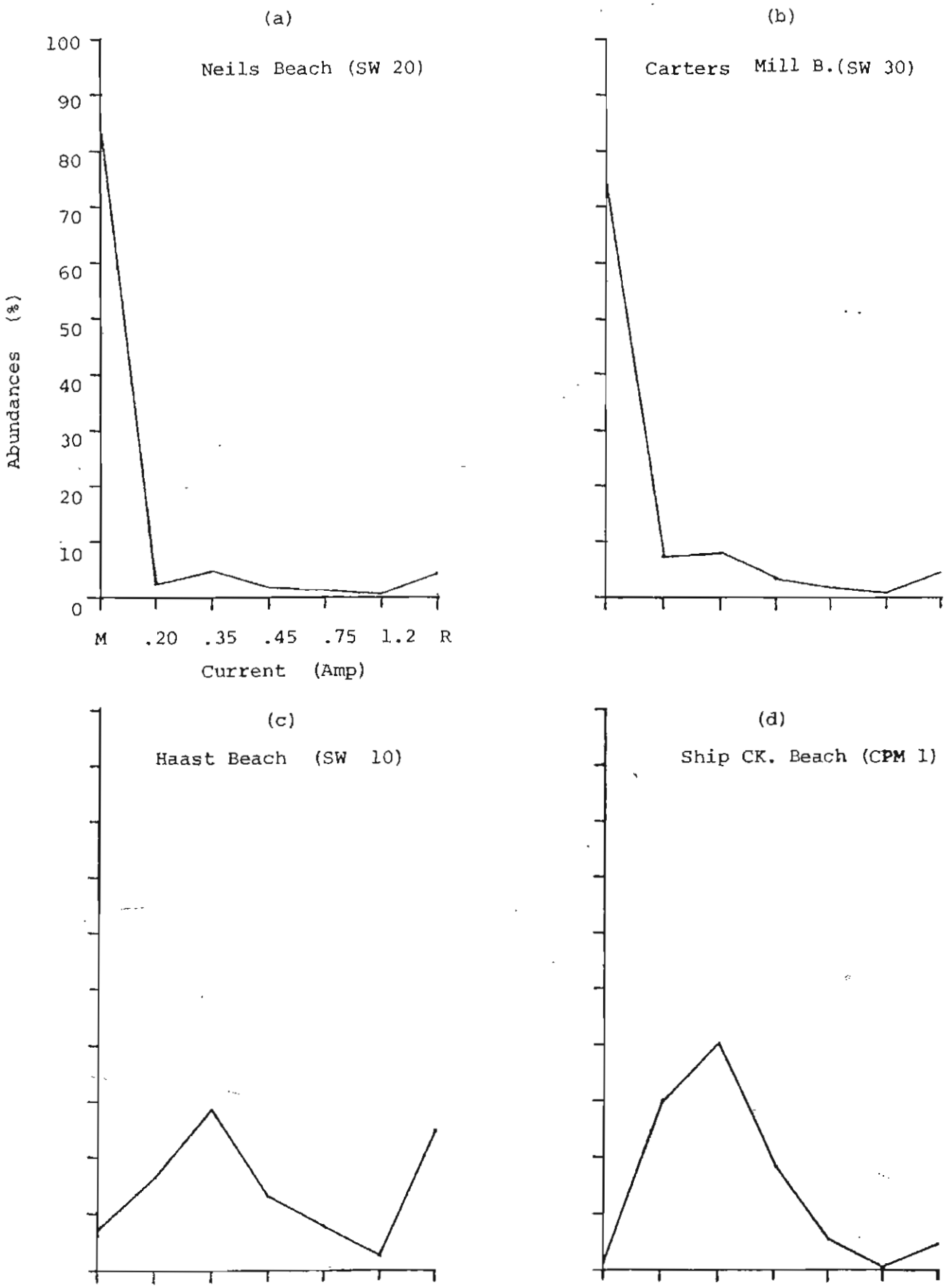
IV SIGNIFICANCE OF MAGNETIC RESPONSE PROFILES (MRP)

A plot of the mineral abundance (percentage weight of magnetic cuts) versus the magnetic susceptibility (amperage) of a sample, gives the Magnetic Response Profile (described in Bradley, 1977). The magnetic response profiles for beachsands in this region reflect the high proportion of magnetite, often greater than 50% of the total heavy minerals. However, moving from south-west to north-east along this beach the general trend is towards increasing proportions of ilmenite and the MRP at Ship Creek beach becomes much more closely similar to that of the heavy beachsand minerals from the typical schists of the Central Westland region (Fig. 7).

The MRPs for 3ϕ river sediments are unfortunately rather misleading. Because of the situation peculiar to this region wherein most of the magnetite is carried down the rivers (especially the Waiatoto and Okuru) in coarse form, the MRPs do not reflect the higher proportion of magnetite. This situation is unusual so far as the general Westland is concerned but it does indicate the need for caution in using MRP.

FIG. 7

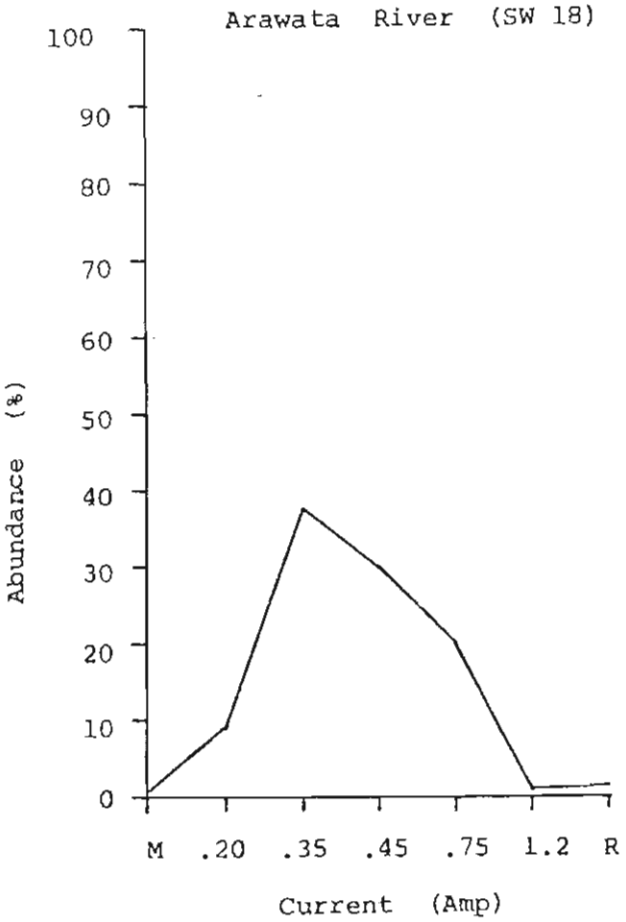
MAGNETIC RESPONSE PROFILES - BEACHSANDS AND RIVER SEDIMENTS OF JACKSON BAY - HAAST AREA



M = Magnetite
R = Reject (non-magnetic)

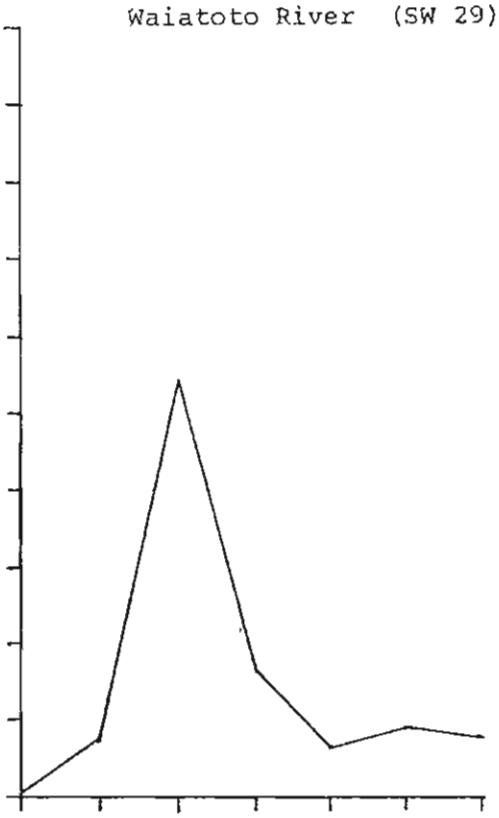
(e)

Arawata River (SW 18)



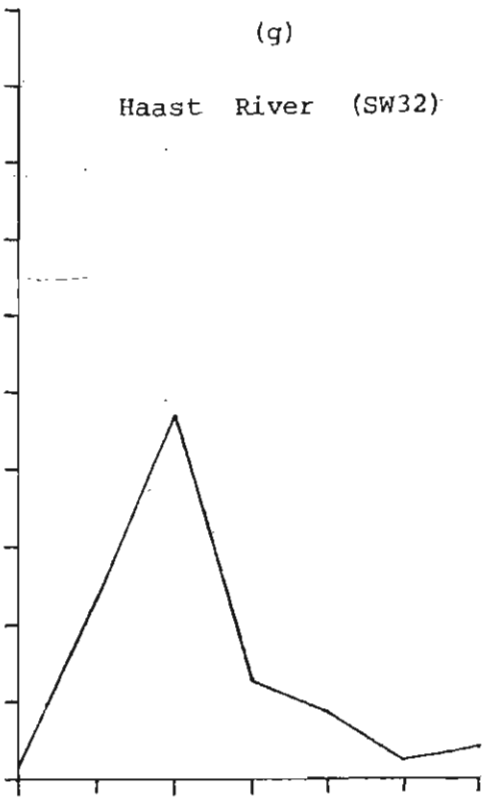
(f)

Waiatoto River (SW 29)



(g)

Haast River (SW32)



V OTHER REMARKS

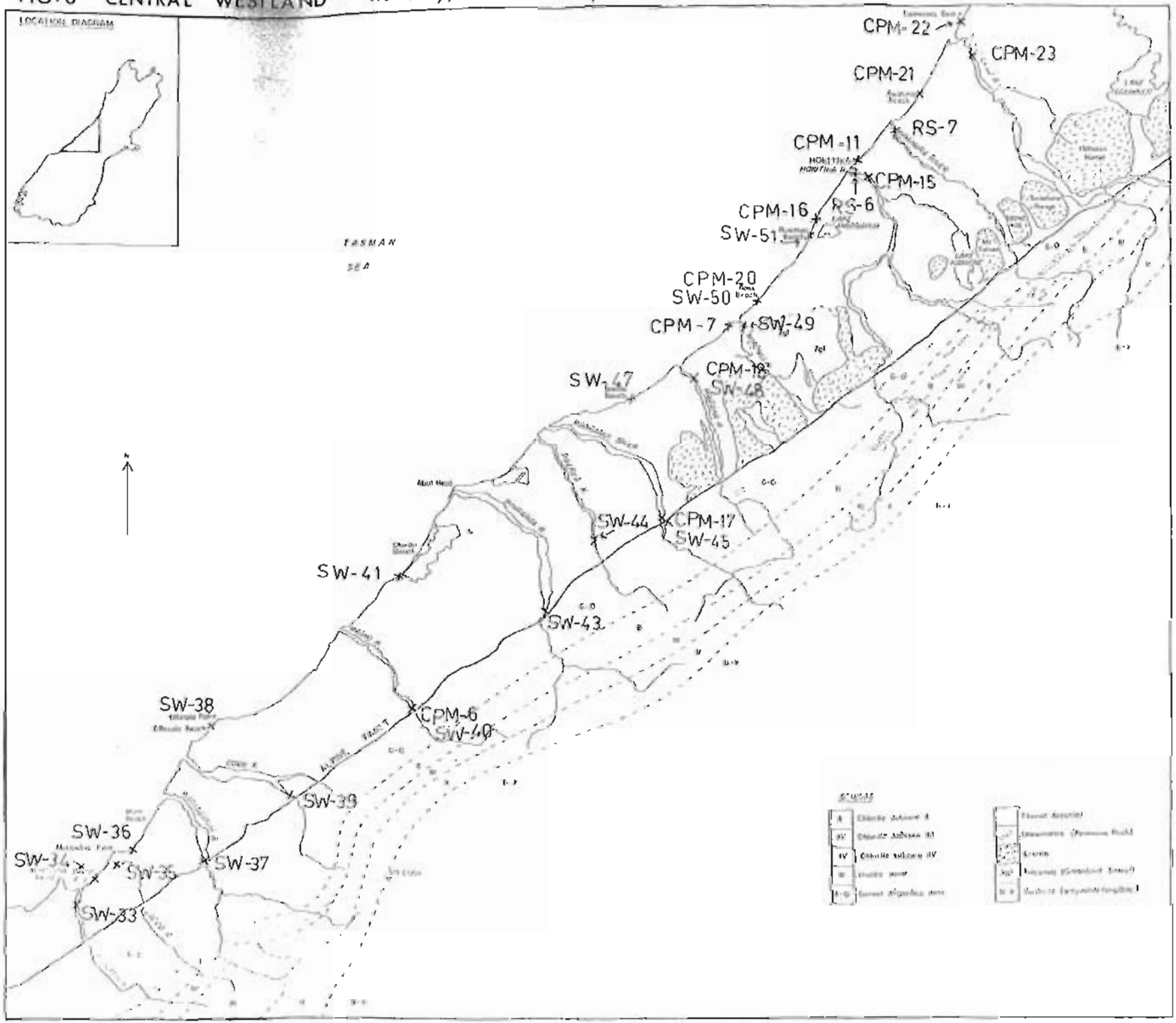
The coastal region south-west of Jackson Head is rather rugged with only isolated pockets of sandy beaches. Although only a few samples from this area were available, the high chromium content of the ultramafic magnetite enables equally its westwards dispersion towards the more southern coast to be followed. Magnetite from the Cascade Rivermouth showed 3·6% chromium which corresponds closely with the value of 3·7% for a sample from the river itself. A sample from the moraine at Iota Bluff, on the south-western side of the rivermouth, gave 3·3%. And Gorge River, further to the south-west, showed 2·9% while a sample from the Bay had 3·4%. As has been pointed out, this coastal magnetite is not finding its way along the coast into Jackson Bay,

The occurrence of gold on the beach north of the Haast River (Table 4:3, sample SW11) has been known since 1867 (May, 1962). With north-eastwards movement of sediments in this region, it is a reasonable inference that the source of this gold lies within the Haast catchment. This stretch of beach provides conditions favourable to its concentration, as evidenced by considerable variations in blacksand concentration and composition, indicating reworking and reconcentration of heavy minerals (perhaps through a shifting balance between access of flood discharge sediments and their coastwise dispersal).

Features of the coastal physiography in the region are also consistent with longshore transport of sediments. There is evidence of beach erosion south of Mussel Point and of aggradation north of Haast River. Dune ridges parallel with the coast in the vicinity of Haast are considerably higher (Ca 30 m) than the south. Moreover, the characteristics of

the Jackson Bay shoreline which lies hard against the rocky coast in the south must be controlled by the prevailing north-eastwards transport of Arawata sediments.

FIG. 8 CENTRAL WESTLAND - Rock types and sample locations



CHAPTER V

CENTRAL WESTLAND

I GENERAL FEATURES OF THE REGION

For the present work Central Westland broadly lies between the Paringa and the Taramakau Rivers. The narrow coastal strip, between the shore and the schist belt, is composed of morainic accumulations, together with glacial outwash of gravels or tills. These are remnants of the Pleistocene and Holocene glaciations and they consist of Alpine Schist rocks, Torlesse greywacke and argillite from close to the Main Divide, and granite from local sources (Guyon, 1967). Numerous rivers draining the Alpine Schists emerge from deep "saw-tooth" gorges to flow across the coastal strip. In the south the Paringa, Mahitahi and Jacob Rivers do not extend to the Main Divide, but the larger rivers take their sources from snowfields and glaciers along the Divide. From south to north the Karangarua, Cook, Whataroa, Wanganui, Hokitika, Arahura and Taramakau Rivers may be listed. North of the Wanganui massive granitic plutons dominate the coastal strip. Within the Waitaha-Taramakau region the Pounamu Ultramafic Pods intrude into the schists (see Fig. 8).

Behind the beach-fronts at Bruce, Hunts, Gillespies and Okarito are undulating aeolian dune sand deposits. These are usually of low relief, elongate and semi-parallel to the coastline. Behind some of these deposits are swamp-type environments overlying fluviatile sands and gravels. Often these dunes are eroded as revealed by the scars and scarps on their seaward sides. At Bruce Bay, for example,

TABLE 5 : 1

MAGNETITE AND ILMENITE CONTENTS IN BEACHSANDS[a] - CENTRAL WESTLAND

Locality	Code	% Heavies in 3ϕ Cut	Magnetite % of Heavies	Ilmenite % of Heavies	I:M Ratio
Bruce Bay[b]	SW 34	91.0	0.91	43.3	47.7
Hunts Beach[c]	SW 36	99.3	3.2	40.9	12.7
Gillespie Beach[d]	SW 38	23.0	3.5	7.7	2.2
Okarito Beach[e]	SW 41	4.0	1.3	28.4	22.0
Greens Beach[f]	SW 47	94.4	0.49	31.67	65.2
Ross Beach[g]	CPM20	96.2	0.93	17.7	19.1
Mahinapua Beach[h]	CPM16	95.8	1.3	22.2	17.1

[a] The percentages refer to 3ϕ sieve fractions from samples collected close to high tide mark.

[b] Sample was from the northern side of the Mahitahi Rivermouth.

[c] About 4 km north-east of Jacob Rivermouth.

[d] About 5 km north-east of Cook Rivermouth.

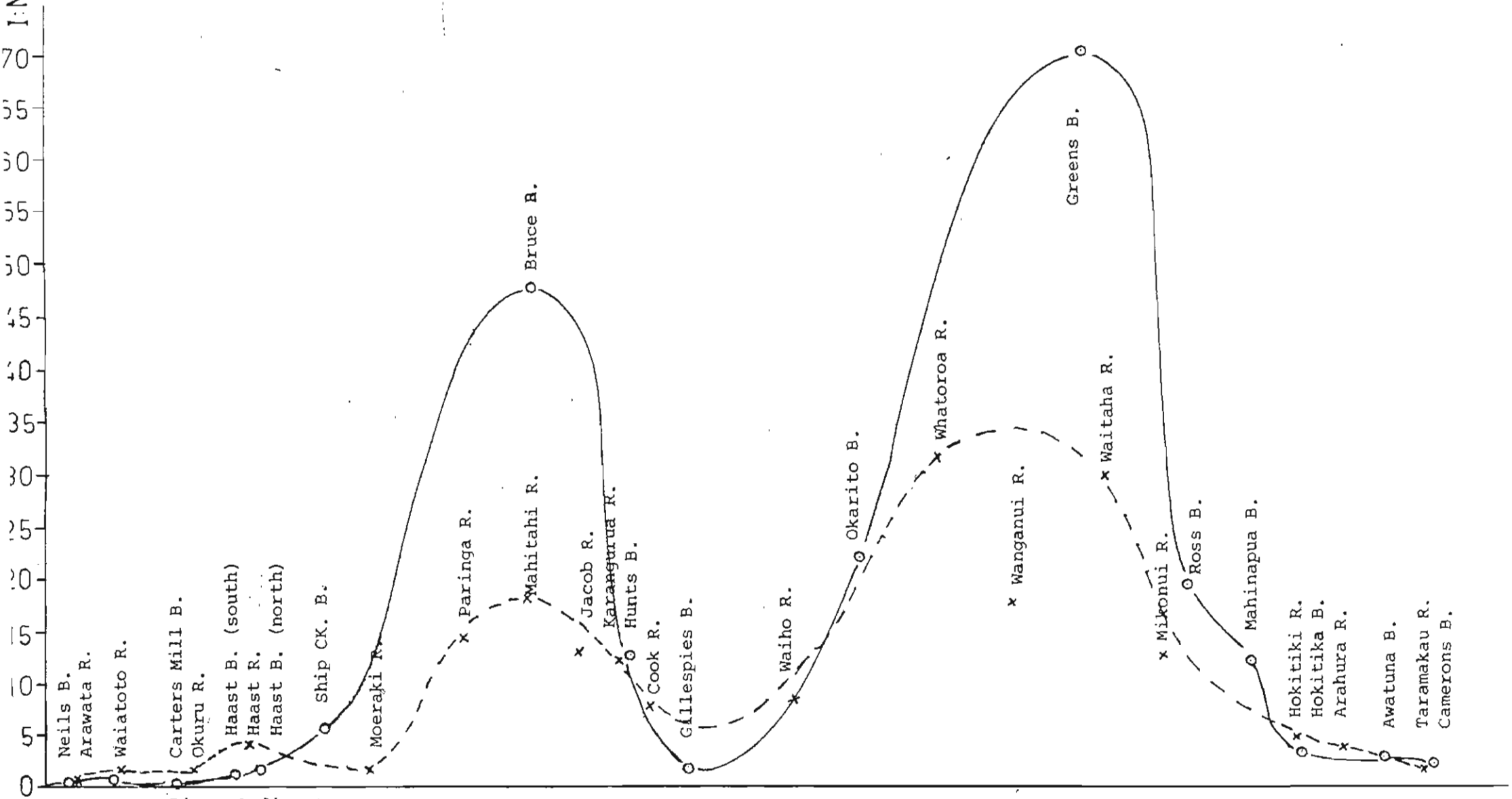
[e] At the south-western end of Okarito Lagoon.

[f] Approximately midway between Wanganui and Waitaha Rivers.

[g] At Ross township.

[h] At Rautapu township.

FIG. 9 PLOT OF ILMENITE:MAGNETITE RATIOS OF BEACHSANDS AND RIVER SEDIMENTS BETWEEN JACKSON BAY AND CAMERONS BEACH



sections of the dunes have been washed away exposing scarps of 3-4 m in height. In these places the beachsand is unusually black, through recent re-concentration.

II RELATION OF BLACKSAND ON BEACHES TO RIVER SEDIMENTS

Unlike the beachsands in the Jackson Bay-Haast area where the magnetite is in greater abundance than the ilmenite, the Central Westland beaches carry proportionately more ilmenite than magnetite (see Table 5:1 and Fig. 4). This trend is apparent from the results reported by Nicholson et.al. (1958). The results from the present work confirm this general trend, but raise the question as to reasons for the variations in the ilmenite and magnetite proportion in the modern beachsands.

The chromium values of magnetite from beachsands and river sediments from the area south of the Waitaha are generally low, but to the north the values are higher and more variable. The significance of this will be discussed in pp (65). However, one line of evidence that relates the beachsands to the river sediments is the variation of the ilmenite:magnetite ratios over the region. For the purpose of making this correlation only the 3ϕ size cuts have been utilised.*

The curve, (Fig. 9), for the ilmenite:magnetite ratios of beachsands from this region shows that the ratios vary considerably from the south to the north.

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* There is difficulty in matching river sediments to beachsands because of particle size. The 2ϕ cuts contain a high proportion of composite grains. Beachsand heavies are predominantly of 3ϕ with lesser amounts of 2ϕ. River sediments on the other hand are mainly of 3ϕ and 4ϕ. To eliminate composite grains, i.e. to obtain mono-mineralogical grains, matching was made only with the 3ϕ cuts.

Thus, in the Bruce Bay region, the ratio is high but falls to a low value in the Gillespies Beach region and rises again to a maximum at Greens Beach, north of the Wanganui River,before falling again to the north. These broad variations relate fairly closely to the variations found for the rivers in the corresponding regions (Fig. 9). Therefore, it can be inferred that the differing ratios reflect regional differences in the ilmenite and magnetite contents of the schists from south to north. The match in the ratio data in the rivers and modern beachsands would indicate that the supply to the beaches has been derived predominately from rather local sources and that in this region of the coast the effect of the longshore drift from the south has not been so great as to obscure this correspondence.

Between Paringa and Waitaha the coastline is frequently disrupted by morainic bluffs, giving rise to lengths of beach that are isolated from one another. The foots of these bluffs usually contain little or no sand and thus must impede the northward longshore transport at the present time. There is possibly some connection between the development of arcuate embayments at both Bruce Bay and Hunts Beach, and the lack of accession of beachsand from the south, past the Teretaniwha and the Makowhio Points. It must be remarked in this connection that coastal erosion of morainic formations must themselves make some contributions to the supply of beachsands, additional to that supplied by the rivers. But again, there is no significant modification of the beachsand heavy mineral content. The morainic tongues extending out from the Alpine Fault are composed of the same 'local' rocks that provide the detritus in the present river beds. But in any case, the role of coastal erosion is greatly slowed by

the massive nature of the greywacke morainic blocks that often accumulate at the base of these cliffs.

On the basis of present information, it is not possible to draw any conclusion as to the proportion (if indeed any at all) of the present beachsand being derived from the beach or dunesands accumulated on the continental shelf through Holocene transgression of a rising sealevel over a coastline that was once about 120 m lower (Carter, 1975). But again, it is clear that any such factor has not modified the correspondence between modern beach and river sediment compositions. In view of the huge discharge of most West Coast rivers, any ironsand concentrated on the shelf during lower stands of sealevels, would have been covered by the modern sediments.

One feature revealed by Fig. (9) is that in regions where ilmenite:magnetite ratio in the river is already high (as in Mahitahi-Jacob, Whatoroa-Waitaha regions), the beach-sand ratio is found to be even higher. No firm suggestion can be offered in explanation of this effect. At Bruce Bay the sea is actively eroding dune sand and concentrating heavy minerals on the beach, but there seems no reason to suppose that this would alter the ilmenite:magnetite ratios. The particle sizes, densities and (at least short term) persistence characteristics of the two minerals are quite similar. Although the Carpentaria Exploration Reports revealed that the ilmenite contents predominate over magnetite in most dune deposits with varying ratios down with depth, as far as surface dune sand accumulation is concerned, there is no systematic difference in the ilmenite:magnetite ratios of the dune sands and the present beaches. For example, at Hunts Beach the ilmenite:magnetite ratio for the present beach sample was 12.7, and a sample from a spot 2 m deep in

the dune deposit (Sb2) gave a figure of 10.9. At Gillespie Beach the present beachsand recorded a ratio of 2·2 and for the dune sand at a depth of 2 m (Sb5) showed 1·9.

It can be inferred from the ilmenite:magnetite ratios of the river sediments from the Central Westland region that the schists there, in general, are ilmenite-rich and rather poor in magnetite. Table 5:2 and Fig. (10). But so far as Cook River is concerned, the higher magnetite content in the sediments, giving rise to a smaller ratio (7·9), would directly indicate the localised occurrence of magnetite-rich zones in the schists. Overall, there is a marked change from the magnetite-dominated schists of the Jackson Bay-Haast region to the ilmenite-rich schists of the Central Westland region.

III CHEMICAL EVIDENCE ON ORIGIN OF MAGNETITE

Along the beaches from Bruce Bay to Greens Beach the chromium content of the magnetite lies generally in the range 200-450 ppm. Figures in this range are in sharp contrast to the high chromium values shown by magnetite from the coast south of Jackson Head and the similar a magnetite distributed from the mouth of the Arawata (pp. 42). There is thus an abrupt change in chromium value of 1150 ppm for the beach at Ship Creek to 200 ppm at Bruce Bay. Chromium contents in the 150-500 ppm range are typical of magnetite from the Alpine schists. The magnetite samples for the beaches between Bruce Bay and Greens Beach, lie. within the above range, as would be expected if there were no accession of magnetite from other chromium-rich sources. These low beachsand chromium values are fully in line with

TABLE 5 : 2

MAGNETITE AND ILMENITE CONTENTS OF RIVER SEDIMENTS

Locality	Code	% Heavies in 3 ϕ Cut	Magnetite % of Heavies	Ilmenite % of Heavies	I:M Ratio
Waipara R.	SW 22	6.5	0.16	0.24	1.5
Arawata R.	SW 18	5.1	0.53	0.27	0.51
Jackson R.	SW 17	8.0	5.2	0.12	0.023
Waiatoto R.	SW 29	6.1	0.28	0.41	1.46
Okuru R.	SW 31	1.8	0.75	1.18	1.6
Haast R.	SW 32	0.42	2.2	8.2	3.7
Moeraki R.[a]	SW 13	3.7	1.7	2.4	1.4
Paringa R.[b]	SW 12	13.1	0.89	12.6	14.2
Mahitahi R.	SW 33	4.5	0.77	13.6	17.7
Jacob R.	SW 35	7.2	0.42	5.7	13.6
Cook R.	SW 39	7.5	3.4	26.0	7.7
Karangurua R.	SW 37	3.2	1.5	18.4	12.2
Whataroa R.	SW 43	5.3	0.27	8.4	31.1
Wanganui R.	SW 45	4.4	0.82	14.6	17.8
Waitaha R.	SW 48	7.6	0.42	12.5	29.8
Mikonui R.	SW 49	7.0	2.1	26.4	12.5
Hokitika R.[c]	RS 6	-	-	-	4.1
Arahura R.[d]	RS 7	-	-	-	3.4
Taramakau R.[e]	-	-	-	-	1.6

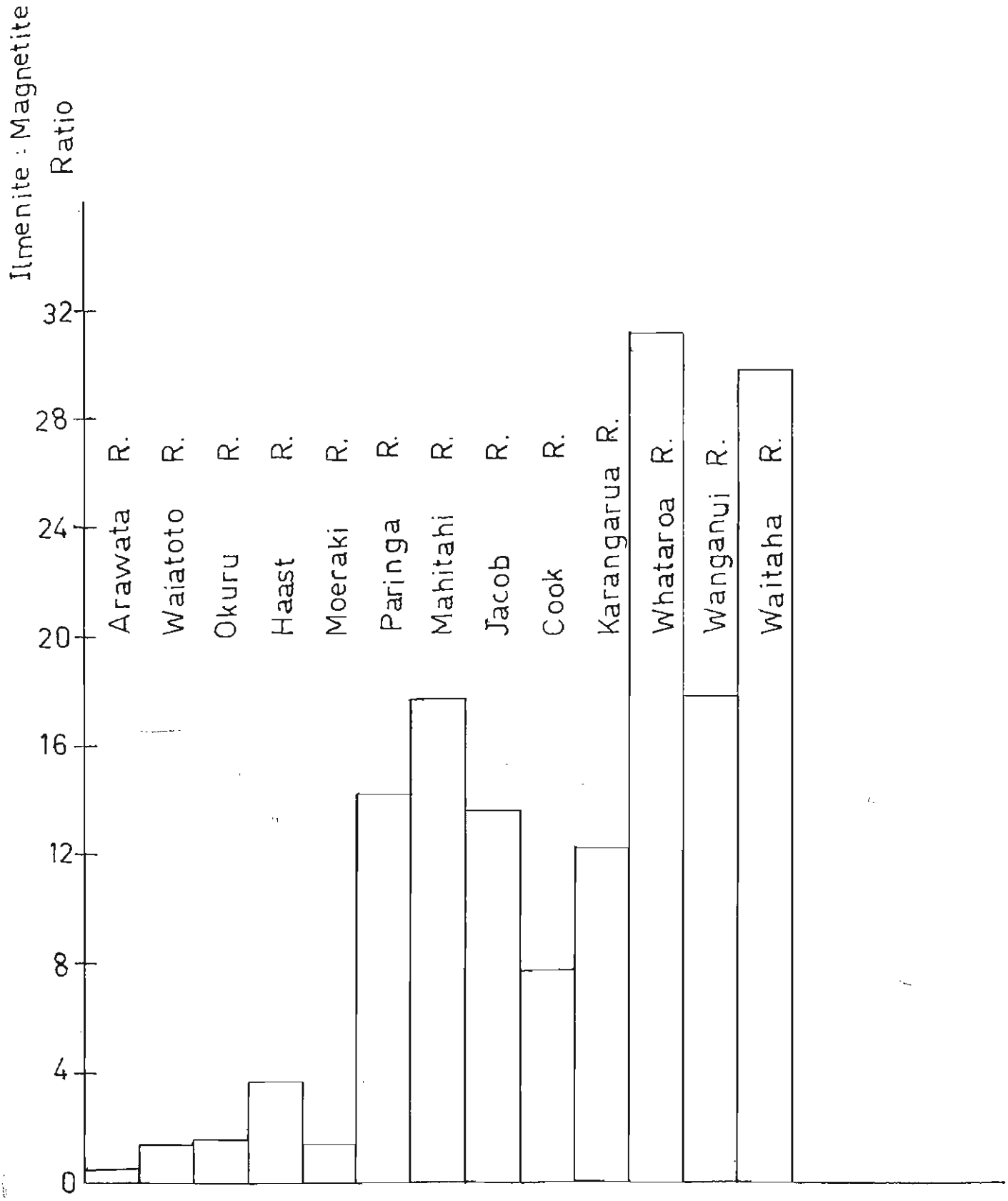
[a] Sample collected at about 50 m from Road Bridge over the Boulder CK.

[b] At the Road Bridge (SHW6)

c,d,e. Ratios derived from Bradley (1977).

FIG. 10

Ilmenite: Magnetite Ratios of Westland River Sediments in South - North Direction (3ϕ).



the low chromium values from the river-borne magnetite in the region Fig. 11. Complete analytical data on the other minor elements in magnetites from beachsands and river sediments from this region are presented in Tables 5:3 and 5:4 respectively.

It may be worth noting that the magnetite from three dunesand samples analysed within this area all gave chromium values almost twice as high as the magnetite from adjacent beaches (see Table 5:3). It is probable that in some beaches, contributions of these dunesand magnetite, in addition to the low chromium magnetite supplied by the rivers, may have slightly raised the overall chromium content.

Magnetite from beachsand samples collected north of the Waitaha River and along the coast past the mouths of the Hokitika, Arahura and Taramakau Rivers, show much higher chromium content. It is of particular interest that the Pounamu Ultramafic pods are mapped as extruding the schists within the catchment areas of these rivers. (Cooper, 1976). As usual, it is to be expected that ultramafic rocks would carry magnetite of high chromium content, and not surprisingly the riversand magnetite samples from these rivers showed high chromium values. There is, thus, a complete correspondence in the northern Central Westland area between sources of supply of the chromium-rich magnetite, its transport down river and accumulation in the beachsands. Hence, again, there is evidence, of a purely chemical kind, that the modern beach from south of Ross to north of the Taramakau carries heavy minerals derived directly from the rivers. In accordance with the effect of a longshore drift from the south-west,

the chromium contents of the magnetite from the beaches on the northern sides of these rivers show higher values than those from the south. Although the Waitaha is relatively small and therefore only a lesser contributor to the beachsand, the chromium content of the sample collected some 7 km north of the river mouth was 1220 ppm, whereas a sample from Greens Beach, which is to the south-west, carried only 440 ppm of chromium and a sample from the rivermouth itself gave a figure of 5900 ppm. Magnetite, from the Lower Hokitika River, gave a chromium figure of 12,700 ppm. While on its south side a value of 1050 ppm was obtained, the north side gave a value of 9100 ppm. A rather different situation arises for the coast between Arahura and Taramakau. The magnetite from beaches north of Arahura (at Awatuna) and Taramakau (at Camerons) gave respective values of 7600 and 4800 ppm. The fall in chromium content is apparently due to the dilution from lower chromium magnetite supplied by these two rivers. The rather lower values from these two rivers, for example 1800 ppm for the lower Taramakau River, could reflect both the smaller proportion of chromium-rich magnetite from the ultramafic pods and increased contribution of low-chromium magnetite from the considerable areas of granites within their catchment areas (Bradley et.al., 1979). Nevertheless, it is clear from the chromium figures that sediments from the rivers are mobilised to the northern sides of the rivermouths.

This extra supply of magnetite from the granites in this northern Central Westland region is also clearly reflected in the lower ilmenite:magnetite ratios of sediments from the Hokitika, Arahura and Taramakau and the adjacent beachsands.

FIG. 11 CENTRAL WESTLAND - Chromium Values (ppm) of Magnetites.

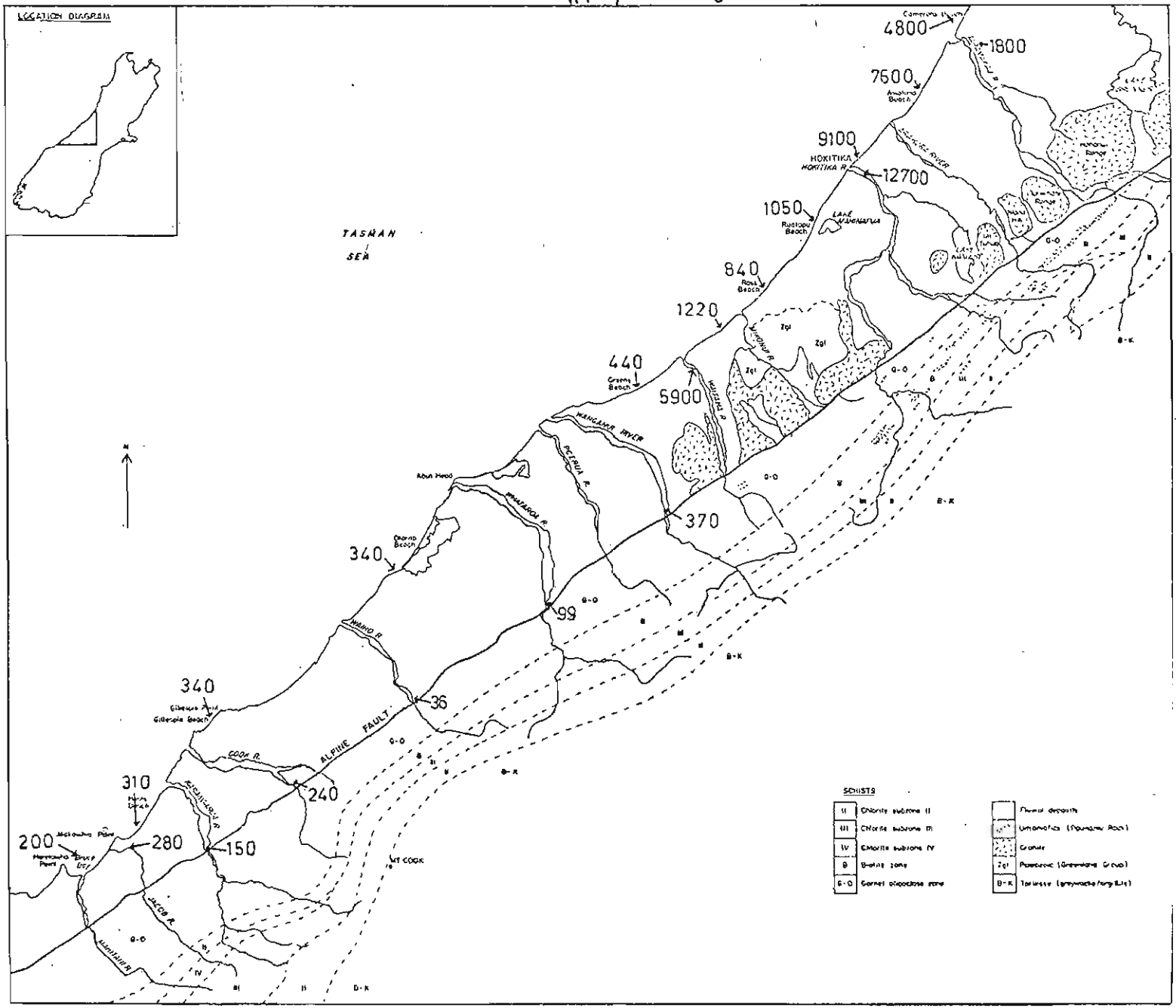


TABLE 5 : 3

MINOR ELEMENT CONTENTS OF MAGNETITE FROM CENTRAL WESTLAND BEACHSANDS AND DUNESANDS (ppm)

Locality	Code	Ti	V	Cr	Mn	Ni	Cu	Zn	Mg
Bruce Bay	SW 34	4090	1490	200	606	172	17	149	447
Hunts Beach	SW 36	2630	1370	311	559	194	7	77	238
Dune deposit 2m[a] deep	Sb 1	1670	1130	570	678	245	10	99	-
Gillespie Beach	SW 38	2790	1360	343	456	204	7	66	333
Dune deposit 2m[b] deep	Sb 5	3190	1280	598	590	270	11	98	-
Okarito Beach	SW 41	3540	1520	338	718	226	9	93	327
Dune deposit 2m[c] deep	Sb 6	4360	1310	655	1190	278	14	109	-
Greens Beach	SW 47	8570	1560	438	1740	251	9	115	522
South of Mikonui Rm	CPM 7	3340	1500	1220	1140	324	10	123	959
Ross Beach	CPM 20	5760	2020	838	1560	235	12	113	968
Mahinapua B.	CPM 16	5500	1930	1050	1590	304	10	127	726
North Hokitika Rm[d]	CPM 11	2020	1170	9110	1200	1104	12	108	4970
Awatuna B[e]	CPM 21	2380	1180	7630	1310	1020	16	125	7000
Camerons B.	CPM 22	5250	1620	4790	1430	607	12	104	2130

a, b, c. Magnetite samples were taken at depth of 2m in the dune deposits at the respective localities.

[d] About 2 km north-east of Hokitika Rivermouth.

[e] About mid-way between Aratuna and Taramakau Rivermouths.

TABLE 5 : 4

MINOR ELEMENT CONTENTS OF MAGNETITE FROM CENTRAL WESTLAND RIVERS (ppm)

Locality	Code	Ti	V	Cr	Mn	Ni	Cu	Zn	Mg
Jacob R.	SW 33	5040	1620	284	401	759	177	115	1070
Karangurua R.	SW 37	1930	476	154	329	1850	187	114	560
Cook R.	SW 39	5280	1580	241	513	647	117	78	1040
Waiho R.	CPM 6	402	ND	36	99	2960	446	163	777
Whatoroa R.	SW 43	545	334	99	136	2330	599	144	917
Wanganui R.	CPM 17	1920	1540	371	2120	384	63	138	658
Waitaha R.	CPM 18	2800	1340	5850	1140	822	22	144	2970
Lower Hokitika R.	CPM 15	2440	1510	12740	1100	2000	29	124	18620
Lower Taramakau R.	CPM 23	8300	2270	1800	1250	234	18	118	2060

IV SIGNIFICANCE OF MAGNETIC RESPONSE PROFILES (MRP) FOR CENTRAL WESTLAND

The MRPs for some rivers and beaches of the Central Westland area are shown in Fig. (12) a... f. The profiles for some rivers, as well as beaches for adjoining areas, are grouped together as composites where similiarities gave justifications for this. Agreement feature of the MRP over the whole area is the low proportion of magnetite in both the river and the beaches as has already been noted (pp. 59, 62). Any significant difference in profiles, for example the rather low proportions of ·45 to Reject cuts of the beaches as compared to the rivers or the change in peak positions of the river profiles, can be explained through

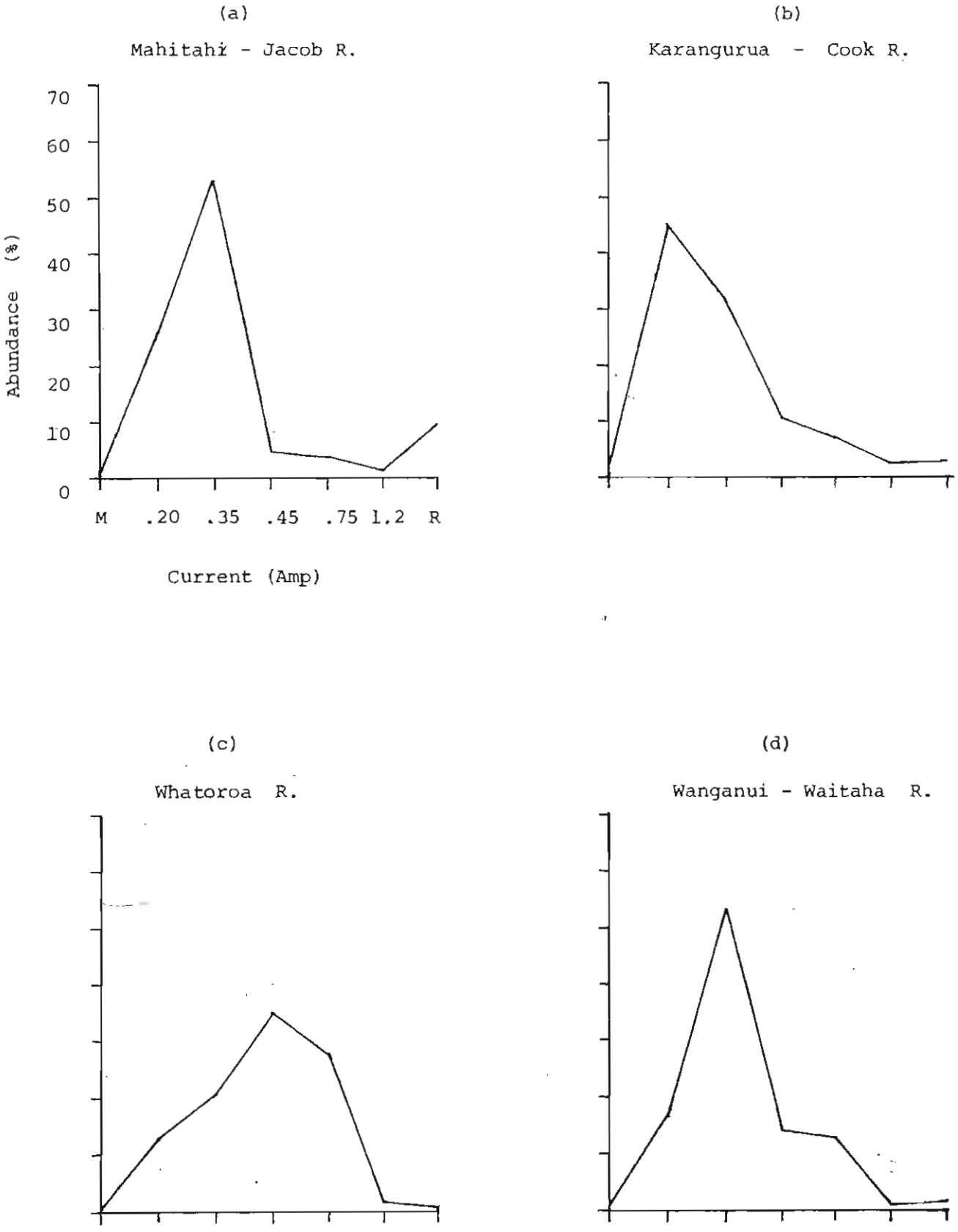
(i) Differences due to disappearance of less persistent minerals such as lencoxene, muscovite and hornblende on the beach, and

(ii) sometimes because of larger than usual variations in the proportions of lencoxene, biotite and epidote in the river samples.

As for the beachsands, the MRPs for Bruce-Hunt-Gillespie and Greens-Ross-Ratuapu, bear strong resemblence to each other having maximums at the ·35 Amp cuts and differed strongly with the MRP for Neils-Carter Mill-Mussel Point (Fig.12g) (Jackson Bay-Haast area) which shows a maximum for the magnetite fraction. Here, again, there is some indication that rock sources of the heavy minerals of the Central Westland beaches are somewhat different from those that supply the Jackson Bay-Haast coast.

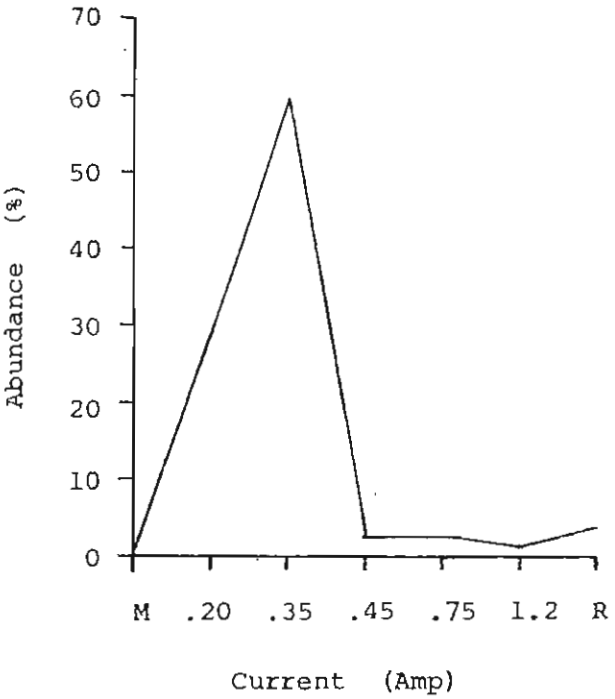
FIG. 12

MAGNETIC RESPONSE PROFILES - BEACHSANDS AND RIVER SEDIMENTS OF CENTRAL WESTLAND



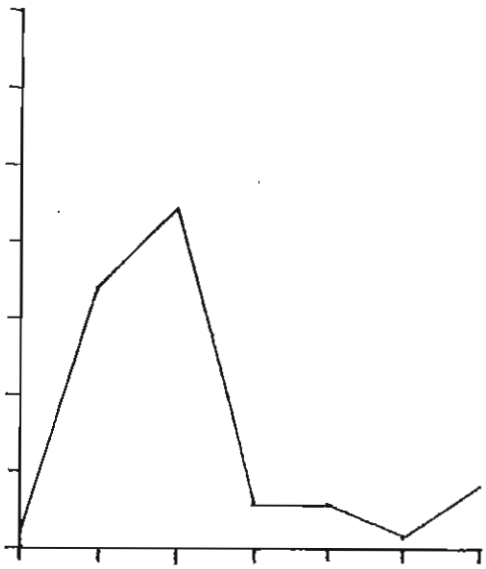
(e)

Rautapu - Ross - Greens B.



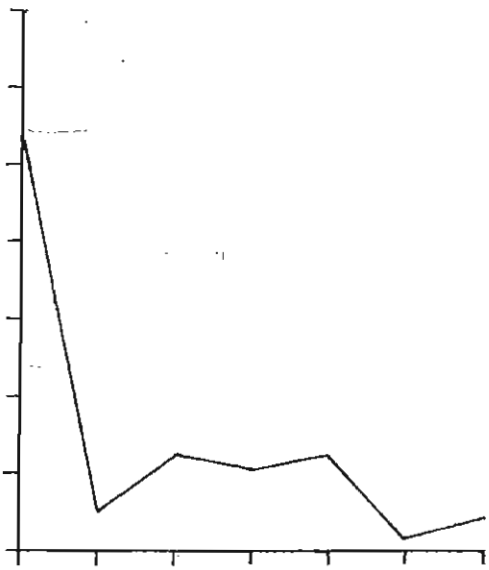
(f)

Gillespies - Hunts - Bruce B.



(g)

Neils - Carters Mill - Mussel Pt.



V PRESENCE OF SULPHIDES

Weak sulphide mineralisations within schists is not uncommon. It shows up as a regional effect in some river source detrital samples from South Central Westland. Especially within the Waiho and Whatoroa, and to a smaller extent the Cook and Karangurua Rivers, the occurrence of sulphides primarily as pyrrhotite (FeS) is noteworthy. This must reflect a higher than usual sulphide content of the schists in this particular region. The ferromagnetic properties of pyrrhotite mean that this mineral is not easily separated from magnetite and no particular effort was made to separate them. It is characteristic of copper and nickel, that because of their capacity to coordinate with sulphides, they are concentrated in pyrrhotite. Therefore, the high copper and nickel figures recorded for "magnetite" from Waiho, Whatoroa, Jacob, Karangarua and Cook Rivers are a direct consequence of pyrrhotite contamination (see Table 5:4). Optical examination of the magnetite samples indicated that except for some 10-15% pyrrhotite for Waiho and Whatoroa Rivers, pyrrhotite contents of magnetite fraction from other rivers, e.g. Jacob, Kaiangurua and Cook, were less than 1% (see Table 8:3) While the very small proportion of pyrrhotite would increase the apparent copper and nickel contents of magnetite fraction from these rivers, its presence would not alter the contents of other minor elements (V , Cr, Ti, etc.) substituting in the magnetite lattice to any appreciable extent. But for higher proportions such as in the Waiho and Whatoroa samples, the figures obtained for the other elements are slightly reduced.

On the whole the presence of sulphides in the river detritals in no way complicates the situation regarding sources and accumulation patterns for the heavy detrital minerals. Pyrrhotite and other sulphides generally are non-persistent and do not accumulate on beaches.

VI GOLD IN CENTRAL WESTLAND BEACHES

In the present study no deliberate attempts were made to identify sources of beachsand gold, especially since it accumulates predominately in the finer fractions (<4ϕ) that are generally not examined. Nevertheless, there is sufficient background evidence for some comments to be made on beachsand gold accumulation. Apart from known occurrences at Bruce Bay, beaches at Gillespies and Okarito (Carpentaria Exploration Reports), the only identifications of gold were in the <4ϕ fraction for the Karangurua River and from the beachsand north of the Haast River.

The known widespread occurrence of fine beachsand gold on the Westland coast from the Haast River northwards, suggests rather widespread sources of supply. In addition to the rich localised sources of gold in the Greenland series at Ross, Waiata and Reefton (and hence the gold-rush fluvial-glacial deposits at Hokitika, Arahura and Taramakau Rivers) it can be suggested that the Alpine Schists contain sparse gold in many places. It is gold from this latter source which has been concentrated in the blacksands but the richer beachsand sources are in areas where there is reworking, with consequent second-stage concentration of gold from older beachsands and dunes.

Thus, at Bruce Bay where there is active erosion of older materials, the reconcentration on the present beach

is attractive to prospectors. The beach immediately to the north of the Haast Rivermouth,where gold was also identified, was commented on in the previous Chapter page 53.

CHAPTER VI

NORTH WESTLAND BEACHSANDS

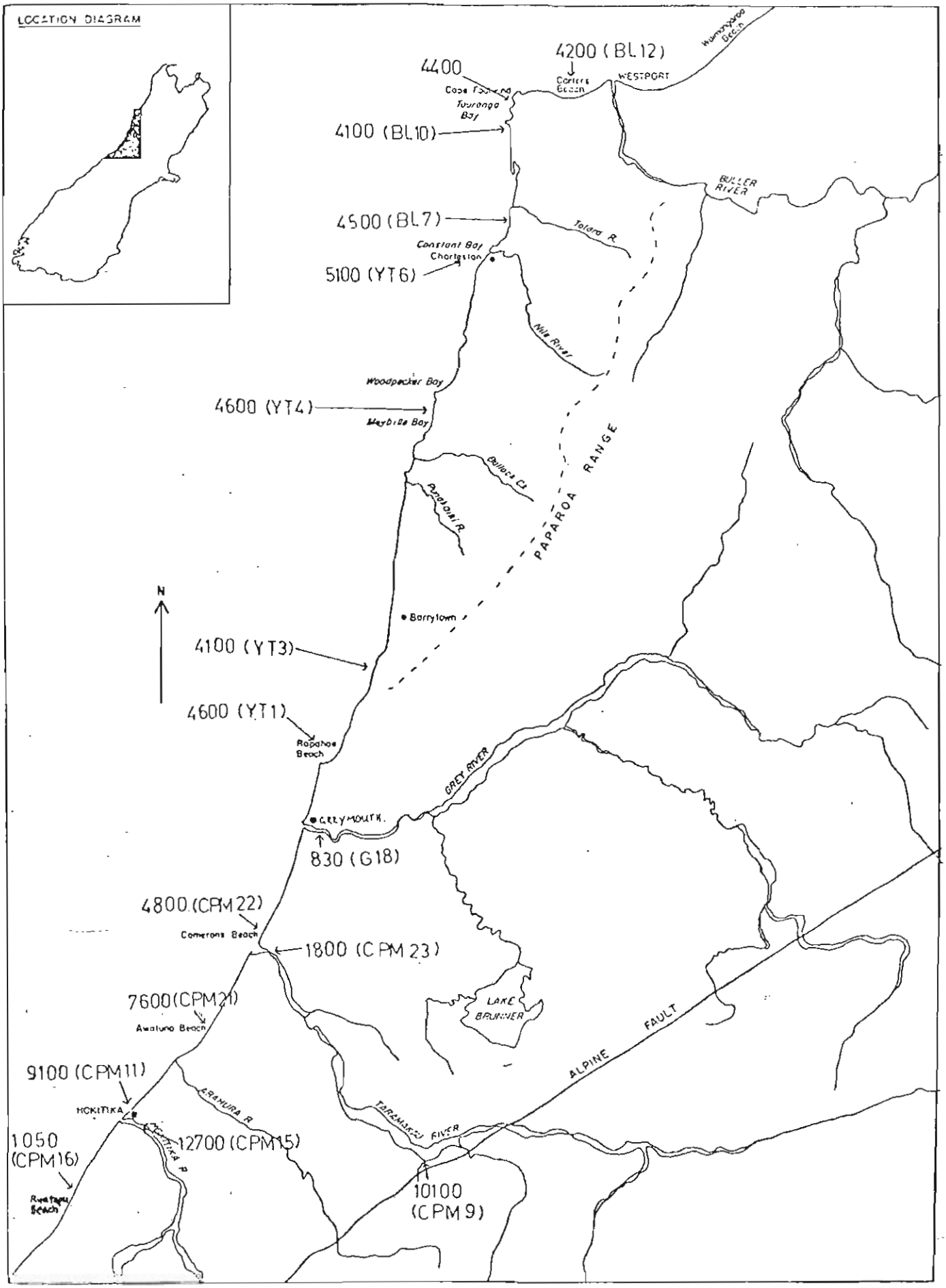
I SETTING OF THE AREA

For purposes of the present study this area is taken as lying between the Taramakau River and the Buller River to the north. The main geographical feature is the Paparoa Range which consists essentially of granite (probably distinct from the Tuhua formation), Constant Gneiss and a Greenland Group sedimentary block. Along the coastline itself are small outcrops of Constant Gneiss, but more importantly in terms of detrital mineralogy, there is a series of interglacial marine terraces in the Charleston-Cape Foulwind area (McPherson, 1978). The main rivers are the Grey,whose drainage area covers the eastern flank of the Paparoa Range and the Victoria Range, and the Buller which drains rocks of diverse origin, including the Paparoa granites. A number of short and small rivers have their origins on the western flank of the Paparoa Range and flow westward to the sea.

In some sheltered areas behind the modern beaches (notably at Barrytown) there are accumulations of dunesands and beach gravels which carry blacksand leads. Estimations of ilmenite accumulates at a number of places - Barrytown, Nine Mile Beach and Carters Beach - run into millions of tonnes (Martin, 1955). On the present active foreshore of these beaches, the sand bears varying proportions of blacksand and the wave action has often concentrated these heavy minerals into leads containing up to 45 percent ilmenite (McPherson, 1978).

FIG. 13

CHROMIUM CONCENTRATIONS (ppm) IN MAGNETITE FROM NORTH WESTLAND



II CHEMICAL EVIDENCE ON ORIGIN OF BLACKSAND

The present survey confirms the occurrence of varying proportions of iron minerals in the beachsands (Table 6:1). It seems unlikely that these iron oxide minerals have been derived from local rock sources since the Constant Gneiss, Greenland Sedimentary block and the granites of the Paparoa Range are themselves all rather poor sources of iron oxide minerals. The work of Smale and Nathan (NZGS Report G-36, 1980) shows that sediments derived from the basement rocks in and around the Paparoa Range are dominated by mica-apatite-ziron assemblage and are generally poor in magnetite and ilmenite.

McPherson (1978) provides mineralogical evidence to show that the blacksands are predominantly derived from the more southern beaches (the Central Westland beaches in particular) which in turn received their supply from the Alpine Schists. These heavy minerals have subsequently been concentrated by coastal processes and transported by effective northwards longshore drift. This movement of sediments has been remarked upon by Furkert (1947) for the Westport area.

Analytical data on minor element concentrations in magnetites, accumulated in this survey, provide a quite independent line of evidence on the derivation of blacksands from the more southern beaches. Magnetites from beaches in this region show chromium values that are remarkably uniform, lying in the 4000-5000 ppm range (Fig. 13). In the previous discussion on provenance of the blacksand on the beaches (pp. 66) it has been pointed out that the compositions (with special reference to the chromium values)

of magnetite between Ratuapu and Camerons Beach vary with the input of characteristic magnetites supplied by the Hokitika, Arahura and Taramakau Rivers. It can, however, be seen from Table 6:1, that the minor element concentrations in magnetites along the Paparoa coast up to Cape Foulwind correspond closely to the composition of magnetite from the Camerons Beach area, just north of the Taramakau Rivermouth. It is thus apparent that the Taramakau River marks the northernmost major contributing source of magnetite to the coastal beaches. Evidently the "mix" of magnetite from the Taramakau, Arahura and Hokitika Rivers and from the beaches to the south is being transported without compositional variation along the Paparoa Coast. It is also probable that the bulk of the ilmenite and garnet on the North Westland beaches has been carried northwards in the same manner as the magnetite from the more southern beaches.

Although the Grey River has a large catchment draining rocks that include the granites of the Paparoa Range and Victoria Range, there is no evidence that the sediments carry sufficient magnetite to alter the picture. A magnetite sample from the lower Grey gave a chromium value of 830 ppm but the chromium content of magnetite from Rapahoe Beach (4600 ppm) on its northern side was not significantly affected.

III REMARKS ON RELATIVE PROPORTIONS OF ILMENITE AND MAGNETITE

The scope of this work and time available were not such as to enable any systematic assessment of the significance of the ilmenite:magnetite ratios in beachsands north of the Taramakau. However, results available do point to some interesting features. The low ilmenite:magnetite ratios for

the beaches just north of the Hokitika, Arahura and Taramakau, are directly due to contributions of magnetite from the granitic plutons and the ultramafic pods in their catchment areas. But at Rapahoe Beach some 5 km north of the Grey, the ilmenite:magnetite ratio is higher than that of the Camerons Beach and further north the ratios increase steadily (Table 6:2). The reasons for this trend have not been determined (although it is understood that subsequent efforts will be made in this direction).

The amount of ilmenite being contributed by the Grey has not been established although its magnetite contribution is known to be low. As remarked above, there is no evidence of important accession of magnetite and ilmenite in the smaller rivers draining the western flank of the Paparoa Range. But to the north in the Charleston-Buller area, the rising ratios may represent some supply from ilmenite-rich sands in the raised beaches. It is appropriate to note that according to McPherson (1978) the blacksands on the raised terraces have, in the past (mainly late Pliestocene), also have been derived from the Alpine Schists. As yet, only one sample from the Mitchells Mine near Charleston has been examined. The yellow-stained magnetite gave a chromium value of 3770 ppm which is comparable to the values of magnetites from the modern beaches.

A possibility which cannot be dismissed, is that over a lengthy period of transport, there may be preferential loss of magnetite over ilmenite through attrition. Certainly no such effect becomes apparent in the beaches to the south since in the southern region the beachsands are not isolated from sources of supply of river sediments in the same way as the beachsands of the Paparoa Coast.

On the other hand, if the transport of beachsand to the north is slow, the rising ratio, especially in the Cape Foulwind area, may reflect the high ilmenite:magnetite ratio of sediments input from the Hokitika-Taramakau region at an earlier stage. It is conceivable, for example, that during periods of heavy glaciation, a larger proportion of the detrital minerals was derived from the Alpine Schists than from the outlying granites - with consequent increase in the supply of detrital ilmenite relative to magnetite, in the North Westland region.

TABLE 6 : 1

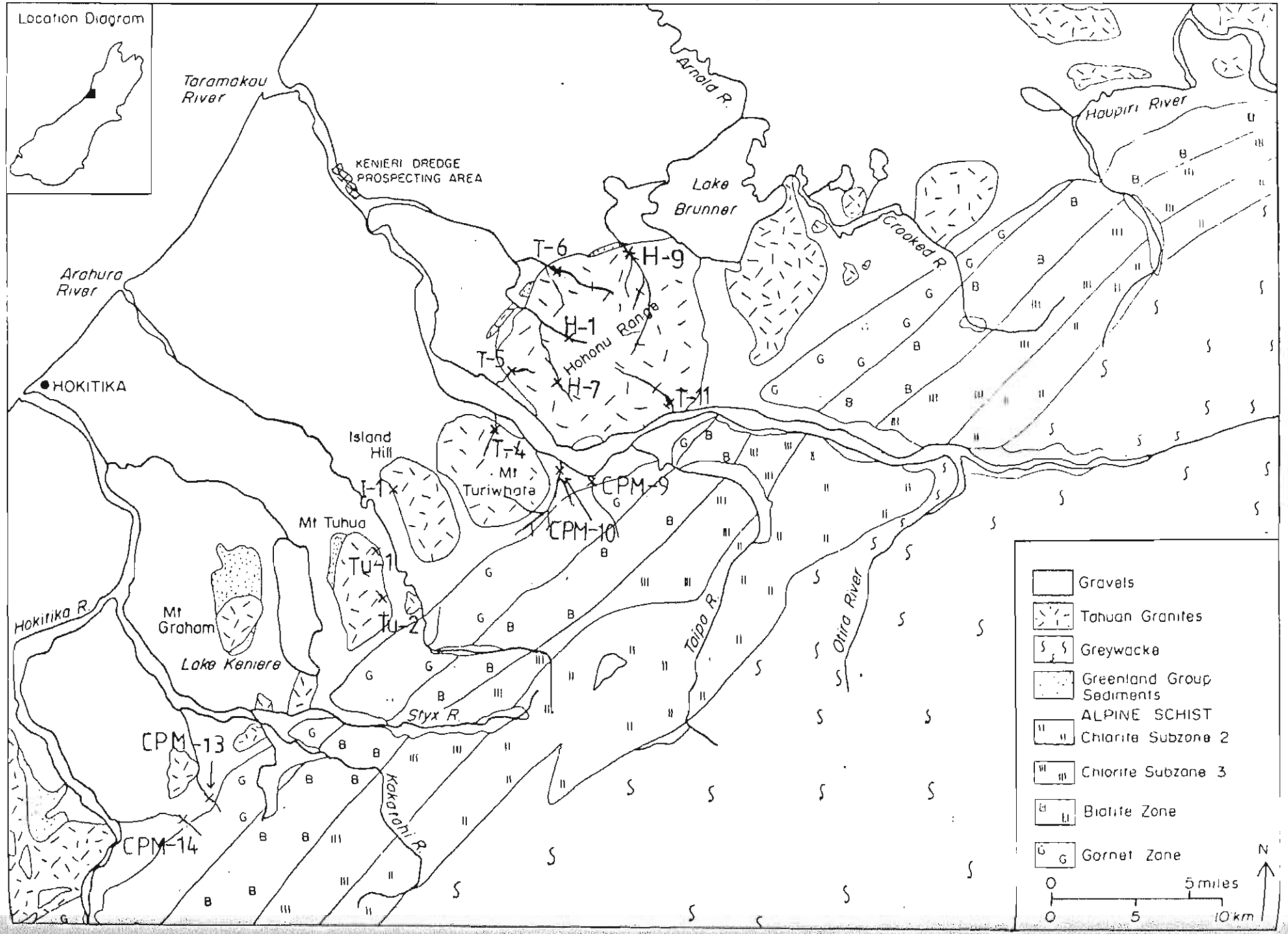
MINOR ELEMENTS IN MAGNETITES FROM NORTH WESTLAND BEACHES

Locality	Code	Ti	V	Cr	Mn	Ni	Cu	Zn	Mg
Awatuna B.	CPM 21	2380	1180	7630	1310	1020	16	125	7000
Camerons B.	CPM 22	5250	1620	4790	1430	607	12	104	2130
Rapahoe B.	YT 1	3500	1540	4590	1640	568	26	172	2490
Koraroa Ck.B.	YT 3	6760	1580	4060	1270	572	14	156	2620
Meybille Bay	YT 4	5890	1640	4640	1410	599	11	168	2040
Nine Mile B. (south end)	BL 7	6880	1350	4490	1350	683	16	136	-
Nine Mile B. (north end)	BL 10	6730	1450	4050	1360	800	16	169	-
Tauranga Bay	-	2.5%	1400	4400	2370	673	23	143	-
Carters B.	BL 12	5690	1710	4250	1180	673	24	153	
Lower Grey	G 18	3440	687	828	1960	282	184	-	2650
Mitchells Mine (Charleston)		3960	1590	3770	1120	480	10	96	1560

TABLE 6 : 2

ILMENITE:MAGNETITE RATIOS FOR 3ϕ CUTS OF NORTH WESTLAND BEACHSANDS

Locality	Sample Code	% Heavies in 3ϕ Cut	Magnetite % of Heavies	Ilmenite % of Heavies	I:M Ratio
2 km north side of Hokitika Rivermouth	CPM 11	93.00	3.36	11.15	3.31
Awatuna Beach (7 km north of Arahura Rivermouth)	CPM 21	95.16	5.86	15.99	2.73
Camerons Beach (2 km north Taramakau Rivermouth)	CPM 23	98.10	7.47	17.76	2.37
Rapahoe Beach (5 km north Grey Rivermouth)	YT 1	66.0	0.69	4.09	5.93
Meybille Bay	BL 4	28.0	0.38	2.40	6.24
Joyce Bay	-	-	1.68	18.42	11.51
Nine Mile Beach (south end)		51.0	0.57	9.56	16.82
Tauranga Bay		87.30	0.56	14.43	23.52
Carters Beach		76.60	0.67	14.36	21.32


Location Diagram
Taramakau River
Arnold R.
Haupiri River
KENIERI DREDGE PROSPECTING AREA
Lake Brunner
Crooked R.
Arahura River
T-6
H-9
H-1
Hohonu Range
T-5
H-7
T-11
HOKITIKA
Island Hill
T-4
Mt Turiwhata
I-1
CPM-9
CPM-10
Mt Tuhua
TU-1
TU-2
Mt Graham
Lake Kenirere
Hokitika R.
Taipo R.
Otira River
Styx R.
CPM-13
CPM-14
Kokatahi R.
Gravels
Tahuan Granites
Greywacke
Greenland Group Sediments
ALPINE SCHIST
Chlorite Subzone 2
Chlorite Subzone 3
Biotite Zone
Garnet Zone
N
0 5 miles
0 5 10 km

CHAPTER VII

MINOR ELEMENTS IN MAGNETITE AND ILMENITE FROM SCHIST AND GRANITE ROCKS

In considering data of these kinds, various comparisons can be made provided complications do not intervene. Perhaps one of the more important aspects has been to use the characteristic minor elemental composition of magnetite to follow dispersal and accumulation patterns of sediments. This assumed particular importance both in South Westland and North Westland because a portion of the magnetite is derived from ultramafic sources and the present work has established that the chromium content of ultramafic-derived magnetite is very high in relation to that of magnetite from other sources, whether they be schists or granites. In South Westland and Central Westland local variations in the concentration of the other minor elements were sometimes too great to enable them to be used to follow transport patterns. But in North Westland, knowledge of minor element contents of magnetite has provided useful back-up information to follow movement of blacksand northwards towards Cape Foulwind.

To establish such information it was necessary however to carry out a large number of analyses for minor elements in magnetite samples from both schists and granites. (See Fig.14 for localities of the granite samples). At the same time, with ilmenite as well as magnetite available from some bulk samples, a number of ilmenite samples were also analysed.

Results of magnetite and ilmenite analysis are

TABLE 7 : 1

MINOR ELEMENT CONCENTRATIONS (ppm) IN MAGNETITES FROM SCHIST, GRANITE AND ULTRAMAFIC ROCKS

	Locality	Sample Code	Ti	V	Cr	Mn	Ni	Cu	Zn	Mg
SCHIST ROCK MAGNETITE	Waitoto R.	SW 29	1340	1300	200	600	130	13	60	470
	Roaring Billy	-	2400	1400	320	540	160	12	70	400
	Pleasant Flat	-	4000	1350	300	600	160	20	100	1080
	Paringa R.	SW 12	6320	1420	870	610	480	80	130	3400
	Cook R.	SW 39	5280	1580	240	510	650	120	78	1040
	Jacob R.	SW 35	5040	1600	280	400	760	180	120	1070
	Wanganui R.	CPM 17	1920	1540	370	2120	380	63	140	660
	Doughboy CK.	CPM 13	2550	1490	120	1770	160	15	90	670
	Vine CK	CPM 14	2050	1530	130	2350	230	18	130	590
	Waihinihini CK	CPM 10	1130	990	490	1850	690	34	200	800
GRANITE ROCK MAGNETITE	Little Hohonu CK	T-6	4750	2090	570	1000	80	13	94	1030
	French CK.	H-1	5790	2000	440	1090	90	20	110	1970
	Rt.branch, Greenstone CK	H-7	6390	1700	810	760	120	23	100	2110
	Rubislaw CK.	T-11	24240	1300	640	2150	120	29	79	4880
		T-5	1150	1540	450	590	78	13	67	1170
		H-9	15280	2210	660	1820	100	22	80	3660
	Mt.Turiwhate	T-4	3790	3140	1890	530	170	22	80	-
	Mt.Tuhua	Tu-2	4050	2160	1130	560	130	24	97	3660
	Johnson CK.	Tu-1	2090	2710	1180	390	120	22	88	5130
	Island Hill	I-1	12470	1600	510	700	89	32	130	4250
ULTRAMAFIC MAGNETITE	Cascade R.	SW 27	2660	660	36070	3170	920	180	-	46400
	Jackson R.	SW 17	1700	560	9180	1630	2090	90	220	60600

TABLE 7 : 2

MINOR ELEMENT CONCENTRATIONS (ppm) IN ILMENITES FROM ALPINE SCHIST AND TUHUA GRANITE

	locality	Sample Code	V	Cr	Mn	Ni	Cu	Mg
SCHIST ROCK ILMENITE	Paringa R.	SW 12	580	100	7000	195	-	2560
	Gout CK.	SW 6	390	71	10980	185	75	6120
	Cook R.	SW 39	440	53	11100	168	70	2550
	Mahitahi R.	SW 33	460	88	7770	220	112	2370
	Wanganui R.	CPM 17	265	ND	11830	300	132	3260
	Griffin St.	CPM 9	230	240	14560	260	79	2500
	Doughboy CK.	CPM 13	240	59	18130	140	100	2960
GRANITE ROCK ILMENITE	Hohonu R.	H-4	680	505	12760	200	59	3100
	French CK.	H-1	810	410	19320	210	54	2260
	Mt.Turiwhate	T-4	3450	1240	1480	315	60	4940
	Johnson CK.	Tu-1	2790	390	1850	250	66	5250
	Island Hill	I-1	2320	295	3360	185	599	2790

presented in Tables (7:1) and (7:2) respectively, covering titanium, vanadium, chromium, nickel, copper, zinc and magnesium.

I COMPARISON OF MINOR ELEMENT CONTENTS IN MAGNETITES FROM SCHIST AND GRANITE

On the basis of minor element contents, it is generally not possible to distinguish schist-derived magnetite from granite-derived magnetite. This is because of the wide variations of values, particularly those from the granite samples. However, certain general features can be remarked upon.

Titanium. Values from the schist samples cluster mainly in the 1900-6000 ppm range. Samples from the granites do show a broad spread of values but there is clustering in the 3500-6000 range. Some samples carry more than 10,000 ppm and one has about 24,000 ppm.

Vanadium. Vanadium content of schist samples is uniform over the range 1400-1500, whereas in the granite samples the values are higher, lying in the 2000-3000 ppm range.

Chromium. Values of chromium from schist are relatively smaller than those from granites. They lie typically in the 150-600 range. In the granites, however, some values cluster in the 500-600 range and a number in the 1100-1800 range.

Manganese. There is a north-south variation in values for the schist samples. Manganese content of magnetites from South Westland falls in the 500-600 range, while values of samples from North Westland range from 1700-2300 ppm. The

granites also show a similar total spread (500-2200 ppm) but values tend to cluster mainly in the 800-1000 range.

Nickel. Nickel values from schists run typically in the 150-400 range but rise to higher values in regions of sulphide mineralisation. Values from the granite samples are fairly consistent, lying within the 80-130 ppm range.

Copper. Like nickel, higher values for schist samples are recorded in regions of sulphide mineralisation, but typical values lie in the 12-20 range. Copper values from the granites are very uniform also, lying in the 20-30 ppm range.

Zinc. Magnetites from both rock types carry zinc in the 60-130 ppm concentration range.

Magnesium. Schist values fall mainly in the 400-1000 ppm range with one sample reaching 3400 ppm. The granites on the other hand show much broader variations and with values that are higher than those of the schist. These range from 1000 to 5000 ppm.

Similar information can also be extracted from the ilmenites and is presented in the Table below.

TABLE 7 : 3

REPRESENTATIVE VALUES IN ILMENITES (ppm)

	V	Cr	Mn	Ni	Cu	Mg
Schists	250-450	50-100	7000-14,000	150-300	70-130	2500-3200
Granites	600-800 2300-3400	300-500	1400-3300 12,000-19,000	200-300	50-60	2000-5000

General Comment

For the elements vanadium, chromium, manganese and magnesium, the schist samples show values that are more uniform and in some cases relatively smaller than those of the granite samples. Nickel has similar spread of values for both rock types but in the case of copper, the granite samples exhibit more uniform figures than the schist samples.

Discussion

It is apparent that for both minerals the schist samples in general have much more uniform concentration ranges for the minor elements than the granites. These schist values probably represent concentrations which accord with equilibrium conditions because the metamorphic process involved redistribution under static physical conditions over a long time interval. The variations shown by samples from the Tuhua granites very likely reflect fractionation during partial melting, differential cooling and also the heterogeneous nature of the granitic masses.

Ultramafic-derived magnetites

Analysis of magnetites from river sediments has confirmed the association of high-chromium magnetite with the ultramafic rocks. The magnetite samples from the rivers draining South Westland ultramafic rocks have very high chromium contents (Table 7:1). In addition, samples from rivers that drain the Pounamu ultramafics in North Westland and also the isolated exposures in the Okuru area (Cooper, 1976) are found to be rich in chromium as would be apparent from these examples :- Griffin stream (CPM 9) - 10,000 ppm,

Lower Hokitika (CPM 15) - 15,000 ppm, Waitaha River (CPM 18) - 5,800 ppm, Lower Okuru River (SW 31) - 1,700 and Lower Arawata (SW 18) - 5140 ppm. These chromium-rich magnetites, released from the ultramafic rocks into the rivers that drain them, act as chemical tags on the sediments, so enabling their transportation, contribution to sediments and dispersion along the beaches to be broadly followed. It must also be remarked that the ultramafic samples give distinctly high values as well for nickel, copper and zinc. Likewise the magnesium content of magnetite from South Westland ultramafics is extremely high and this is probably a reflection of the high magnesium in the host rocks. However, the limited data do not suggest there is necessarily a close parallel between high magnesium and chromium values.

II DISTRIBUTION OF MINOR ELEMENTS BETWEEN MAGNETITE AND ILMENITE

Most work on distribution of minor elements between coexisting magnetite and ilmenite phases has been on major iron ore deposits. The analyses usually show that vanadium, chromium, nickel and copper have a preference for the magnetite phase and the magnesium and manganese for the ilmenite phase. For example, Lister (1966),in his study of some iron ores of magmatic origin, found that there is 1·5 to 8 times more vanadium and 1 to 9 times more chromium in the magnetite phase than the ilmenite phase. On the other hand, the ilmenite phase has 1 to 6 times as much magnesium and contains 1·5 to 8 times more manganese than does the magnetite. (See also Gjelsvik, 1957).

The present consideration relates to minerals from schists and granite rocks. Although many of the samples, particularly those from the granites, were from small river catchments, there must be a caution against assuming that the magnetite and ilmenite had coexisted in the host rocks. Nonetheless, the availability of both magnetite and ilmenite in the bulk samples permitted some assessment of the distribution of the minor elements between these two oxide minerals.

The minor element contents in magnetite-ilmenite pairs, with their corresponding partition ratios, are presented in Table (7:4). Brief comments on the individual element are given below.

Vanadium. For this element the schist samples show partition ratios that are compatible with published data. The magnetite phase contains 2·4 - 4·9 times as much vanadium as the ilmenite phase. This gives an average of 4·2 which is similar to the value recorded by Gjelsvik (1957) for the Norwegian metamorphosed iron ore deposit. Contrary to expectation, the granite samples show no definite pattern of vanadium, prefering the magnetite phase over the ilmenite phase. In fact, in three samples, the ilmenite phase carries more vanadium than the magnetite.

Chromium. Again, the distribution ratios for the schist samples are in good agreement with known data. Excluding Gout CK, which is undoubtedly peculiar, they range from 2 to 8 in favour of the magnetite. For the granites there is no evidence of chromium showing strong preference for the magnetite phase. The magnetite fraction only contains marginally high concentrations of chromium than ilmenite and in one sample has even less.

Manganese. In all samples from both schist and granite, the ilmenite fractions have relatively more manganese than the magnetite fractions. The high ratios clearly demonstrate the preference of manganese for the ilmenite rather than the magnetite structure.

Nickel. Nickel shows opposing distribution trends for the schist and granite samples. In schist, nickel distribution favours magnetite with ratios ranging from 1·1 to 3·8. This trend is compatible with expected behaviour of nickel. But for the granite samples, nickel occurs in greater abundance in the ilmenite than the magnetite phase. No firm explanation can be offered at this stage for this observation.

Copper. Gjelsvik (1957) found that in the Sunnmore deposit in Norway, copper is preferentially incorporated into the magnetite rather than the ilmenite structure. There is however no evidence that this is so in either the schist or the granite samples. On the contrary, half of the schist and all of the granite samples have ilmenites that contain more copper than the magnetites.

Magnesium. Schist samples conform better with the expected distribution trend of magnesium. Except for one sample which has a ratio close to 1·1, in the others the ilmenite contains markedly more magnesium than does the magnetite. The granite samples, on the other hand, yield ilmenite that contains only marginally more magnesium than the magnetite and in one sample there is even a 1·5:1 ratio in favour of the magnetite.

Overall the schist samples show much better agreement

with known distribution patterns of the minor elements than do the granite samples. Consideration of partition ratios thus provides additional evidence of the more uniform distribution of minor elements in minerals formed under conditions of regional metamorphism. The anomalies exhibited by the Tuhua granite samples undoubtedly are directly reflective of the great variability and complexity of conditions (especially of temperature) during granitisation.

TABLE 7 : 4

MINOR ELEMENT CONCENTRATIONS IN PAIRS OF MAGNETITE AND ILMENITE AND CORRESPONDING DISTRIBUTION RATIOS

	LOCALITY and CODE		Concentrations (ppm)						Distribution Ratios					
			V	G	Mn	Ni	Cu	Mg	V	Cr	Mn	Ni	Cu	Mg
SCHIST	Doughboy CK	M	1490	120	1770	160	15	670	6.2	2.0	1	1.1	1	1
	CPM 13	I	240	59	18130	140	100	2960	1	1	10.2	1	6.7	4.4
	Wanganui R.	M	1540	370	2120	380	63	660	5.9	-	1	1.3	1	1
	CPM 17	I	260	ND	11830	300	130	3270	1	-	5.6	1	2.1	5.0
	Cook R.	M	1580	240	510	650	120	1040	3.6	4.5	1	3.8	1.7	1
	SW 39	I	440	53	11100	170	70	2550	1	1	21.8	1	1	2.5
	Yout CK	M	1180	1940	2020	440	150	-	3.0	27.7	1	2.3	2	-
	SW 6	I	390	70	10980	190	75	6120	1	1	5.4	1	1	-
	Paringa R.	M	1420	870	620	410	83	3400	2.4	8.7	1	2.2	-	1.3
	SW 12	I	580	100	7000	190	-	2570	1	1	11.3	1	-	1
GRANITE	Hohonu R.	M	1430	330	2100	56	18	1510	2.1	1	1	1	1	1
	H-4	I	680	510	12760	200	59	3100	1	1.5	6.1	3.6	3.3	2.1
	French CK	M	2000	440	1090	85	20	1970	2.5	1.1	1	1	1	1
	H-1	I	810	410	19320	210	54	2260	1	1	17.1	2.5	2.7	1.1
	Mt Turiwhate	M	3140	1890	530	170	22	-	1	1.5	1	1	1	1
	T-4	I	3450	1240	1480	310	60	4940	1.1	1	2.8	1.8	2.7	-
	Johnson CK	M	2710	1180	390	120	22	5130	1	3.0	1	1	1	1
	Tu-1	I	2800	400	1850	250	60	5250	>1.0	1	4.7	2.1	3.0	>1.0
	Island Hill	M	1600	510	700	90	32	4250	1	17	1	1	1	1.5
	I-1	I	2320	300	3370	190	59	2790	1.5	1	4.8	2.1	1.8	1

M = Magnetite
I = Ilmenite
ND = Not Detected

CHAPTER VIII

MINERAL ASSEMBLAGE OF HEAVY DETRITALS IN RIVER SEDIMENTS

I GENERAL

Although the present work is concerned mainly with the relative proportions of magnetite and ilmenite in the river sediments and beachsands, and relied on the minor constituents in these oxide minerals, there were also available many processed magnetic fractions from heavy detrital concentrates. Thus, as a supplementary study to provide a more complete picture of the types of minerals being supplied by the rivers to the beaches in Westland, these heavy detrital minerals in the various magnetic cuts were identified as the work progressed. This served also to complement Bradley's investigation of the mineralogy of the Westland beachsands. At the same time, it was felt that the river sediments would be more directly reflective of the host rock-heavy mineral composition and that knowledge of these minerals would be a useful aid in identifying potential source rocks. The detailed petrological studies of the metamorphic schist rocks (Mason, 1962, Reed, 1958) were most helpful in providing information on what to expect in the sediments.

Identifications were by optical examination and,where necessary,confirmation was sought with x-ray diffraction technique (Bradley (1977) gives details in his M.Sc.thesis). In this connection, the help rendered by Mr. G. Davey, Miss J. McLennan (both graduate students in the Geology Department) and Mr. D. Smale of the N.Z. Geological Survey, Christchurch, is gratefully acknowledged. In these mineral identifications,

there was no intention of identifying every detrital curiosity and thus it is possible that minerals of very minor occurrence might have been overlooked. Nevertheless, both sampling patterns and laboratory procedures were such that any signfiicant components within the sediments would not have escaped identification.

The relative proportions of the main constituents vary considerably. Weights of magnetite cuts and their relative percentages for the river samples are included, since this information is necessary to establish the proportion of any individual mineral in a sample, Tables (8:1) and (8:2).

II COMPOSITION OF SAMPLES. TABLES (8:3) and (8:4)

The rivers between the Arawata and Taramakau drain mainly the schist belt and as expected the heavy detritals are characteristic schist minerals. The major constituents are apatite, biotite, chlorite, epidote, garnet, hornblende, ilmenite, magnetite, muscovite, rutile, sphere and zircon. Minerals that occur in variable or minor amounts include carbonate, leucoxene, pyrrhotite, sillimanite, tourmaline and tremolite. The mineralogy of samples from the Jackson, Cascade and Gorge Rivers which drain ultramafic rocks, as well as schists, would be expected to be more complicated. In addition to schist minerals, lesser amounts of anthophyllite chromite, diopside, enstatite and zoisite were also present. For a more complete picture, available information on mineralogical composition of samples from Westland beaches is presented in Table (8:5).

Further comments beyond those made by Bradley (1977) on some minerals are warranted.

Anthophyllite, $(Mg,Fe^{+2})_7Si_8O_{22}(OH)_2$. This was identified in the Jackson and Cascade River sediments and its immediate source would be the Red Mountain ultramafites. The occurrence at Ship Creek beach was probably derived from the adjacent Sardine Terrace sand deposits from which anthophyllite was also identified.

Chromite, $FeCr_2O_4$. X-ray diffraction scans on the magnetite fractions often indicated the presence of chromite in the southernmost rivers, but optically detrital chromite was recognised only in the Gorge River. It occurs in the peridotites and serpentinites of the Red Mountain ultramafites but the apparent absence in the river sediments, as well as the nearby beachsands, can be ascribed to the fine size of the grains.

Diopside, $CaMgSi_2O_6$. Diopside of the Lower Taramakau was most certainly derived from the Tuhua granites and their intrusive dykes. The source of altered diopside from the Jackson River is however less certain.

Enstatite, $(Mg,Fe)SiO_3$. The occurrence of this mineral in the Taramakau and Cascade samples would relate to the ultramafic sources such as the Pounamu pods in the Waitaha-Taramakau schists, and the peridotites or serpentinites of the Red Mountain-Cascade area in the far south. Enstatite detected in the beachsands from Wanganui northwards would probably have originated from the Pounamu pods.

Pyrrhotite, FeS. Its presence in the Wanganui, Waiho and Cook sediments reflects the occurrence of sulphide mineralisation zones within the Central Westland schists. Being paramagnetic, it appeared in the early magnetic cuts.

Sillimanite, M_2SiO_5. Minor amounts of sillimanite were found in the finer size fractions (4ϕ and <4ϕ) of the schist samples from Waitaha, Karangurua, Paringa, and Moeraki. This mineral was probably derived from isolated exposures of high grade metamorphosed rocks in these areas. Identification of sillimanite in Westland schist was significant but not surprising since its presence was already known from the Snowy River and Rimu dredge concentrates (Hutton, 1950).

Tremolite, $Ca_2Mg_5Si_8O_2(OH)_2$. Occurrence of this mineral in the river sediments is closely related to the ultramafic rocks, including intrusions into the schists. It was identified in the "schist" sample from Paringa, but larger amounts were found in the northern and southern rivers. Sparse tremolite was found on the Central Westland beaches, even though it was not identified in the rivers in that area.

Zoisite, $Ca_2Al_3(SiO_4)_3(OH)$. This type of epidote forms the main constituent in several magnetic cuts of the heavy concentrates from Gorge and Cascade Rivers. Zoisite is peculiar to the Red Mountain-Cascade area and its distribution is restricted to the adjacent beaches.

TABLE 8 : 1

WEIGHT OF MAGNETIC FRACTIONS OF HEAVY CONCENTRATES FROM RIVERS

Sample Code	Locality	Size Fraction	Wt.of Sample Floated (g)	Wt of Heavy Mineral (g)	% yield	Wt of Magnetite	Wt of .2 Amp Cut	Wt of .35 Amp Cut	Wt of .45 Amp Cut	Wt of .75 Amp Cut	Wt of 1.2 Amp Cut	Wt of REJECTS
SW 49	Mikonui R.	3+4ϕ	290.00	21.191	7.31	0.433	8.299	10.620	1.200	0.413	0.096	0.137
SW 48	Waitana R.	3ϕ	250.00	18.772	7.60	0.080	3.401	13.048	1.178	0.609	0.141	0.315
SW 45	Wanganui R.	3ϕ	250.00	10.904	4.36	0.090	1.785	3.970	2.365	2.461	0.130	0.103
SW 40	Waiho R.	4ϕ	250.00	6.785	2.71	0.102	1.086	1.203	2.675	1.301	0.190	0.228
SW 39	Cook R.	3ϕ	300,00	22.538	7.51	0.768	13.083	5.479	1.783	0.911	0.149	0.365
SW 37	Karangaria R.	3ϕ	150.00	4.774	3.18	0.072	1.471	1.831	0.588	0.573	0.087	0.148
SW 12	Paringa R.	4ϕ	202.00	26.216	12.97	0.236	4.791	12.102	4.444	2.223	0.454	1.966
SW 13	Moeraki R.	4ϕ	325.20	12.690	3.90	0.074	1.460	7.440	1.138	1.562	0.241	0.783
SW 9	Haast R.	3ϕ	300.00	3.311	1.10	0.048	0.775	1.555	0.440	0.282	0.081	0.126
SW 29	Waitoto R.	3ϕ	250.00	16.640	6.65	0.043	1.256	9.000	2.646	1.038	1.454	1.204
SW 18	Arawata R.	4ϕ	250.00	15.625	6.25	0.219	1.223	5.456	5.769	1.418	0.230	1.310
SW 17	Jackson R.	4ϕ	250.00	10.693	4.27	0.672	0.492	6.897	1.604	0.510	0.075	0.443
SW 27	Cascade R.	<2ϕ	250.00	34.900	13.96	4.91	2.807	16.246	2.785	6.882	0.654	0.404
SW 24	Gorge R.	2ϕ	250.00	95.830	38.33	4.130	3.355	28.041	37.047	20.623	1.233	0.936
	Sardine Terrace	3ϕ	-	19.64	-	-	9.00	8.87	1.22	0.40	0.07	0.15

TABLE 8 : 2

WEIGHT PERCENTAGES OF MAGNETIC FRACTIONS OF TOTAL HEAVY MINERAL WEIGHT

CODE	Wt of SAMPLE (g)	MAGNETITE	.2 Amp	.35 Amp	.45 Amp	.75 Amp	1.2 Amp	REJECT
SW 49	21.19	2.04	39.15	50.10	5.66	1.94	0.45	0.65
SW 48	18.77	0.43	18.12	69.51	6.28	3.24	0.75	1.68
SW 45	10.90	0.83	16.37	36.41	21.69	22.57	1.19	0.94
SW 40	6.78	1.50	16.01	17.75	39.43	19.17	2.80	3.36
SW 39	22.53	3.41	58.05	24.31	7.91	4.04	0.66	1.62
SW 37	4.77	1.51	30.81	38.44	12.32	10.75	1.82	3.10
SW 12	26.21	0.90	18.28	46.16	16.95	8.48	1.73	7.50
SW 13	12.69	0.58	11.50	58.59	8.96	12.30	1.90	6.17
SW 9	3.31	1.45	23.41	46.96	13.41	8.51	2.45	3.81
SW 29	16.64	0.26	7.55	54.07	15.90	6.24	8.74	7.24
SW 18	15.62	1.40	7.84	34.92	36.92	9.08	1.47	8.38
SW 17	10.69	6.28	4.60	64.50	15.00	4.77	0.70	4.14
SW 27	34.90	14.20	8.10	46.90	8.00	19.80	1.90	1.20
SW 24	95.83	4.30	3.50	29.26	38.66	21.52	1.34	0.97
SARDINE TCE.	19.86	-	45.80	45.16	6.21	2.04	0.36	0.76

Table 8:3 Composition of Magnetic Fractions[a] of Heavy Mineral Concentrates from Westland Rivers

	Sample Locality[b]	Magnetite	.2 Amp	.35 Amp	.45 Amp	.75 Amp	1.2 Amp	Non-magnetic
CENTRAL WESTLAND	Lower Taramakau[c] H2	MM	II,G*	GG,II,B	HH,MuMu G*,R*,D*	EE,S, D*,P*,Tr*,B*	SS,Mu,Z, Op*,R*	ZZ,R,S,
	Lower Hokitika R.[d] RS6	MM	II,BB,G	GG,BB,B	EE,C,H,B, G,Mu*	EE,B,Mu, Tr,Pu,L	S,E,Tr,LL, P*,Cl*,R*,Mu	ZZ,S,Ap R*
	Mikonui R. SW49	MM	II,GG,B*,C	G,B,H,EE, C,Mu	EE,H,CC, T*,Tr*	EE,T,R, P*	SS,Mu, E,H,P,R*	SS,Ap,P,Z, Mu,L*,R*
	Waitaha R. SW48	MM	II,GG,B*,C*	B,G,H,EE	EE,H,C,B, Mu,P*,T*	EE,Mu,T,C, P*	SS,Mu,P, R,T*,S*,	S,Ap,ZZ, P*,R*,S*,
	Wanganui R. SW45	MM	II,G,C*,B* E*	BB,H,G,EE I	EE,Mu,H*,B*, T*,P*	EE,L,MuMu T*,P*	SS,L,MuMu Ap,Z*,R*,P*	S,Z,Ap,L, R*,P*,Mu*
	Waiho R. SW40	MM, PoPo	II,PoPo,H, G,L,B*	EE,RR,LL, II,G,H	L,EE,TT, B,R,H,C*	LL,SS,T,P* E	SS,LL,Ap,P, R,T*,Mu*	S,Z,P,ApAp LL,Mu*
	Cook R. SW39	MM,Po*	II,G,BB, C*,E*	EE,G,BB,H, C*,I*,P*,Ca*	EE,C,L, T*,P*,R*	E,Mu,P,L, R*,S*	SS,L,P,R, Mu,Z*	Ap,Z,SS, L,R*
	Karangarua R. SW37	MM,Po*	II,GG,C,B	H,B,EE,CC, GG	EE,T,H,Ca*	EE,S,T,L P*	SS,MuMu,R, T*	Ap,S,Z,R, Mu
SOUTH WESTLAND	Paringa R. SW12	MM	II,C,G,P*	HH,G,EE,C, B*,P*	EE,Mu,H,B*, P*,C*,R*,T*	MuMu,E,T*, P*,R*,S*,Tr*	SS,Mu,R, P,L,S*,Ap	ApAp,SS,ZZ, R,Mu
	Moeraki R. SW13	MM	II,GG,HH, C,R,B*	HH,B,E, G,Mu*	EE,HH,B, Mu,T*,P*,S*	EE,TT,MuMu B*,R*	SS,MuMu, R*,P*	ApAp,S,Z,L, R*,S*
	Sardine Tce[e]	M*	II,GG,H*	GG,H(g),E, II,B,An*	EE,LL,Z, I,R	SS,E,LL, Mu*	LL,S,Mu Tr*	ApAp,Z,S, LL,R*
	Haast R. SW9	MM	I,H,GG,C,E, B*	EE,H,P,Ca, T*,L*,B*	EE,H,P, T*,R*,L*	SS,EE,LL,MuMu P*,R*,T*	SS,L,Z*,R* Ap*,Mu*,T*,P*	Z,Ap,LL S,P*,R*
	Waiatoto R. SW29	MM	HH,II,E,G*	HH,EE,II, L,B	EE(alt),MuMu, LL,I,B(alt)	Mu(alt),L,S (alt) EE	SS,L,Mu, E(alt)I,R*	SS(alt),Ap LL,Mu
	Waipara R. SW22	MM	CC,H,B,I	HH,C,I,B	MuMu,EE, H*,Tr*	MuMu,E,Tr	SS,Ap,Mu	ApAp,Z
	Arawata R. SW18	MM	HH,I,EE,B, G	EE,L,HH,MuMu G*	EE,LL,MuMu I,H	EE(incl),MuMu II,L,T,Tr*	SS,L,Mu E(alt),R*	ApAp,Z L*,R*
FAR SOUTH	Jackson R. SW17	MM	H(g/b),I,E, G,B,R	EE,H(g/b),I, B,Mu,Tr,R*	EE(alt),L, MuMu,H,B,Tr	Mu,L,S, E,An*	SS,L,Mu, R*,D*(alt)	Mu,Z,L,S, P*
	Cascade R. SW27	MM	C,An,G,I E*,H*,R*	EE,H(g/b) I,B,Mu	EE,HH(g/b)	EE,OpOp,ZoZo MuMu,H*	Tr,Zo,Op,S	Z,S,Ap R*,P*
	Gorge R. SW24	MM	CC,B*,G*	CC,Cr,B*	CC,G*	EE,Tr,B	ZoZo,TrTr SS	ZoZo,ZZ,L

An = Anthophyllite; Ap = Apatite; B = Biotite; C = Chlorite; Cr = Chromite, Co = Carbonate; D = Diopside; E = Epidote, G = Garnet; H = Hornblende; I = Ilmenite; L = Leucoxene; M = Magnetite, Op = Orthopyroxene; Mu = Muscovite; P = Pyrite; Po = Pyrrhotite R = Rutile; Si = Sillimanite; S = Sphene; T = Tourmaline; Tr = Tremolite; Zo = Zoisite; Z = Zircon.

[a] The lettering indicates the abundance of each mineral within individual cuts:

XX = Main constituent, > 40%; X = 14-40%; xx = 5-15%; x = 1-5%; X* = < 1%.

[b] For sample localities see Figs 5 and 8.

[c,d] Reproduced from Bradley (1977)

[e] Sardine Terrace, located on the coast 15 km north of Hanat River, has been described by Nathan (1975). It is an interglacial sedimentary bed consisting of Quartz, Micas, Schistose rock-fragments and heavy minerals of which Ilmenite and Garnet predominate.

TABLE 8 : 4

COMPONENTS PRESENT IN HEAVY MINERAL CONCENTRATES FROM WESTLAND RIVERS

MINERAL \ RIVER	Taramakau	Hokitika	Mikonui	Waitaha	Wanganui	Waiho	Cook	Karangarua	Paringa	Moeraki	Haast	Waiatoto	Arawata	Jackson	Cascade	Gorge	Sardine Tce.
Anthophyllite														0	*		0
Apatite		*	*	*	*	*	*	*	*	*	*	*	*		*		*
Biotite	*	*	*	*	*	*	*	*	0	*	0	*	*	*	0	*	*
Chlorite		*	*	*	*	*	*	*	*	*	*				*	*	
Carbonate							*	*			0						
Chromite																*	
Diopside	*													0			
Epidote	*	*	*	*	*	*	*	*	*	*	*	*	*	*	0	*	
Garnet	0	*	*	*	*	*	*	*	*	*	*	0	*	*	*		*
Hornblende	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		*
Ilmenite	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		*
Magnetite	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Muscovite	*	*	*	*	*	*	*	*	*	*	0	*	*	*	*	*	
Orthopyroxene	0															*	
Pyrite	0	*	*	*	*	*	*		*	*	*				0	0	
Pyrrhotite					0	*	0	0									
Rutite	*	*	*	*	*	*	*	*	*	*	*	0	*	*	0		*
Sphene	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		*
Sillimanite				0			0	0	0								
Tourmaline			*	*	*	*	0	*		*	0		*				
Tremolite	0	*	0						0				*	*	*	*	*
Zircon	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Zoisite															*	*	
Leucoxene					*	*	*		*		*	*	*	*		*	*

* = significant amount

0 = trace amount

Table 8:5 Composition of Magnetic Fractions[a] of Heavy Concentrates from Westland Beaches

	Sample Location	Magnetite	.2 Amp	.35 Amp	.45 Amp	.75 Amp	1.2 Amp[b]	Non-Magnetic
CENTRAL WESTLAND	Ruatapu Beach SW51	MM	II,GG	GG,II	G,B,E	EE,B,Pu Mu R*,T*,H*	EE,S,Pu,Op, R	ZZ,S, R*,L*
	Ross Beach SW50	MM	II,GG	GG,II,H*	G,B,EE HH	EE,Pu*,Op* Mu*	EE,S,Op,R, Mu*,Tr*	ZZ,SS, Ap,R*
	Greens Beach SW47	MM	II,GG	GG,II,G*	EE,B,GG	EE,B,Mu, R*	EE,S,RR,Op Pu	ZZ,SS R
	Okarito Beach SW41	MM	II,GG,B, C*	GG,I, C,B*	EE,BB, GG	EE,BB, Pu	SS,E,Ap,Pu Op	ZZ,SS,ApAp
	Gillespies Beach SW38	MM	II,GG,B	GG,I,B B*	EE,B,G,C	EE,S,T*	EE,PuPu,Mu SS	ZZ,S,R,P
	Hunts Beach SW36	MM	II,GG,B*	GG,I,E*	GG,B,EE	BB,E,MuMu R*Pu*	RR,E,S, Tr,BB	ZZ,SS, R
	Bruce Bay SW34	MM	II,G	GG,I,HH	BB,G,E,H	BB,E,G*	SS,EE,MuMu R*,T*	ZZ,S,R
	Tauperikaka Pt.[c] CPM1	MM	II,G,E,H, Mu(alt),B*	GG,EE,LL, I,Mu,H,R	EE,LL,GG R*,An*	LL,S,E, Mu	LL,S,E, MuMu	Z,L,S, ApAp,Mu
SOUTH WESTLAND	Haast Beach SW11 (North)	MM	II,G,C*	GG,II,E	EE,B,P,G Mu,L,T*	EE,B,L, Mu	S,E,L,Mu,R*	ZZ,S,Ap* gold*,Hy*,R*
	Haast Beach SW10 (South)	MM	II,G,E,B,H	G,E,II,HH, B	EE,L,H,B, R*,T*	E,L,MuMu, T*,R*,An*	SS,E,L,Mu	ZZ,S,Ap,L, Mu
	Carters Mill SW30	MM	II,GG,B	EE,G,I,B, H	EE,B,Tr*	EE,B,P*	S,E,Z,R* P*	SS,Z,Ap R*,Hy*
	Mussel Point SW2	MM	II,GG,E,C*	GG,E,B,I	EE,BB,G*,T*	EE,B,T*	SS,EE,R*	ZZ,SS,R Q
	Neils Beach SW20	MM	I,B,G,C	EE,BB,GG I,H,C*	EE,B,Tr*	EE,B,Tr*	SS,E,L,R*	SS,Z,Ap,R* L*
FAR SOUTH	Barn Bay SW23	MM	I,B,G,	EE,BB,G	EE,LL,	EE,Tr,B	EE,S,Tr, T*	ZoZo,SS, L,ZZ
	Big Bay SW25	MM	H,EE,BB, G*	HH,B,E,G	EE,H	EE,Tr,H, T*	EE,Mu,Tr	ZoZo,ZZ,L, TrTr,S,R*

[a]Symbols are as in Table 8:3 and also include the following: Pu = pumpettyite; Hy = Hyacinth.

[b]Epidote in the 1.2 Amp Cut includes the Clinozoisite

[c]Sample was collected from the beach adjacent to the Ship Creek mouth

CHAPTER IX

CONCLUDING REMARKS

Unlike previous studies which were in one way or another orientated towards determining quantities of the blacksands within the coastal deposits, the present work is more concerned with establishing the provenance of these blacksand minerals. Bradley's investigation of the heavy detrital minerals in river sediments from the Taramakau catchment is an example of a recent investigation bearing on the present study. While Bradley's research was in the main restricted to a small area, the present work is broad in geographical scope, covering almost the entire length of the West Coast from Barn Bay in the south to Cape Foulwind in the north. Thus, the sampling plans were designed to provide an extensive rather than a detailed local coverage. A search of the recent literature,by means of the Satellite Dialog access to the Geoarchive Data File, did not reveal any work which was closely comparable in scope and aims.

As was foreseen, the geographical setting with the coast parallel to the Fault does provide a good model. On a regional basis the schists are not uniform. Detrital mineral assemblages from the South Westland schists differ from those for the schists to the north in their relative proportions of ilmenite, magnetite, hornblende, biotite and garnet. It was mainly these variations in the schist belt, together with the presence of ultramafic rocks (Red Mountain and Pounamu series), which enabled dispersion and accumulation of the coastal sediments to be followed. The high

chromium content of magnetite from the ultramafic sources was particularly useful. The use of evidence from the ilmenite:magnetite ratios arising from the regional variation in the schist belt, rests on the basis that the relative proportions of these two minerals in river sediments would remain altered during their transport to the sea and subsequent movement along the present-day beaches. Since these minerals have quite similar persistence characteristics and densities, grains of similar size would not be expected to segregate - at least not in the shorter term. Some complications did arise as in the Jackson Bay-Haast Schists (pp. 41), which also release coarse-grained magnetite.

As the approach was chemically based, considerable preliminary work was devoted to establishing methods for routine analysis of both magnetite and ilmenite (Chapter II). This involved extensive tests on methods for dissolving samples, inter-elemental interference studies, and determination of the best operating conditions on the Atomic Absorption Spectrometer. Although the results have not been cross-checked with other analytical methods (notably XRF), the precautions taken, the sensitivity of the Atomic Absorption instrument, and the reproducibility of results, were such that the results obtained were entirely acceptable.

The most southerly significant occurrence of blacksands (magnetite-rich) in the Jackson Bay-Haast beaches coincides with the southernmost coastal drainage of the schists east of the Alpine Fault. These magnetites are derived primarily from the Alpine Schists, as there is no evidence of significant accession of magnetite from the region south westwards of Jackson Head. The few granite outcrops and Paleozoic

sedimentary blocks in the region are only small contributions of detritals. Within this region there is coastal movement of sediments in the north east direction. However, at the present time, due to disruptions of beach continuity by cliffs and morainic bluffs, there is no ready access of these southern beachsands into the Central Westland beaches. In this central region it has been well established, on a basis of the close match of ilmenite: magnetite ratios of beachsands and river sediments, and the low chromium content of magnetite, that the blacksands on the beaches have been supplied by the hinterland schists and transported down in the adjacent rivers. As for the Paparoa coast, the beaches between Taramakau and Cape Foulwind gain their main supply of ironsand from the general northern region of Central Westland. This north-east movement of detrital sediments along the Paparoa coast is decisively marked since there is a striking constancy in the minor element contents of the magnetites.

For the most part, the evidence on derivation of blacksands on the Jackson Bay-Haast and Central Westland beaches as entirely from the rivers of the regions, relates to the modern beaches and present-day conditions. It does not exclude the possibility that at some earlier period of lower sea-level there may have been sufficient development of beaches south-west of Jackson Head or over the Jackson Bay-Central Westland stretch to enable greater mobility of sediments over the whole region. It may be noted that about 19,000-20,000 y B.P., much of the continental shelf was exposed as sea level was then Ca.120 m lower. The hydraulic and sedimentary regimes took on their modern aspects only about 6500 y B.P. when the sea level approached its

present level (Carter, 1975; see also Carter and Heath, 1975). Nonetheless, the main source of the blacksands would remain with the Alpine Schists, with the plutonic granites (wherever they occur) making a relatively small additional contribution.

x x x x

There are inevitably other lines of inquiry which could arise from present work; e.g. the situation with respect to ilmenite:magnetite ratios in older deposits, of which there are a number in the raised beaches from Greymouth northwards. It can hardly be predicted how useful an examination of other minerals would be in connection with beachsand transport. Monazite is known to occur in the beachsands north of the Grey (Hutton,1950). Possibly electron microprobe studies on this mineral with its varied content of rare earths and thorium might be useful in following dispersal north of the Grey.

In retrospect, it can be said that chemical work has certainly been of considerable assistance in the total problem of beachsand movement.

x x x x

APPENDICES

The Appendices cover quite varied information ranging over detrital burdens of rivers, mineralogical analysis and persistence characteristics of minerals.

Also set out is a description of the HF/H_2SO_4 method for the decomposition of ilmenite. For reasons which are given under the Appendix, this method was not used to decompose ilmenite in the present work. Minor element concentration data of selected beachsand ilmenites analysed with the fusion method are also tabulated.

APPENDIX 1

The information on the discharge of the Westland rivers in the Table below is directly extracted from Carter*. Two sets of discharge rates are available because different assumptions were used in the sediment discharge equations (beyond the scope of present work). Nonetheless, the high discharge of some rivers and the variations in the discharge load from the rivers in general are noted.

RIVER BUDGET (mt x $10^6 y^{-1}$) OF SOME WESTLAND RIVERS

	(a)	(b)
Karamea	0.9	0.6
Mokihini	0.6	1.2
Buller	3.2	5.7
Grey	1.3	1.9
Taramakau	1.9	6.1
Hokitika	2.6	7.2
Wanganui	1.3	3.5
Waiho	1.3	1.8
Karangurua	2.6	3.9
Cook	1.3	3
Haast	7.8	31.7
Arawata	6.5	8.9
TOTAL	31.3	75.5

* CARTER, L. (to be published). "Ironsand in Continental Shelf sediment off Westland, New Zealand - a synopsis". (Advance copy of manuscript kindly supplied by the author), N.Z. Oceanographic Institute, D.S.I.R., Wellington. In this manuscript the estimations on discharge load of rivers have been made by

(a) Griffins (in prep.)

(b) Adams (1978).

APPENDIX 2

STANDARD MESH DIMENSIONS

Size Class*	Phi(ϕ)	Microns	Mesh No.
	- 1.0	2000	60
Very Coarse sand			
	0.0	1000	18
Coarse sand			
	1.0	500	35
Medium sand			
	2.0	250	60
Fine sand			
	3.0	125	120
Very fine sand			
	4.0	62.5	230

* After Wentworth (1922).

The precise definitions of the various Phi units as quoted in this study are as follows :-

2.0ϕ refers to all material which has passed through the 1.0ϕ (500μm) mesh but has been retained by the 2.0ϕ (250μm) mesh, i.e. $250 \leqslant x \leqslant 500\mu$ (x = grain size). Similarly for other mesh sizes.

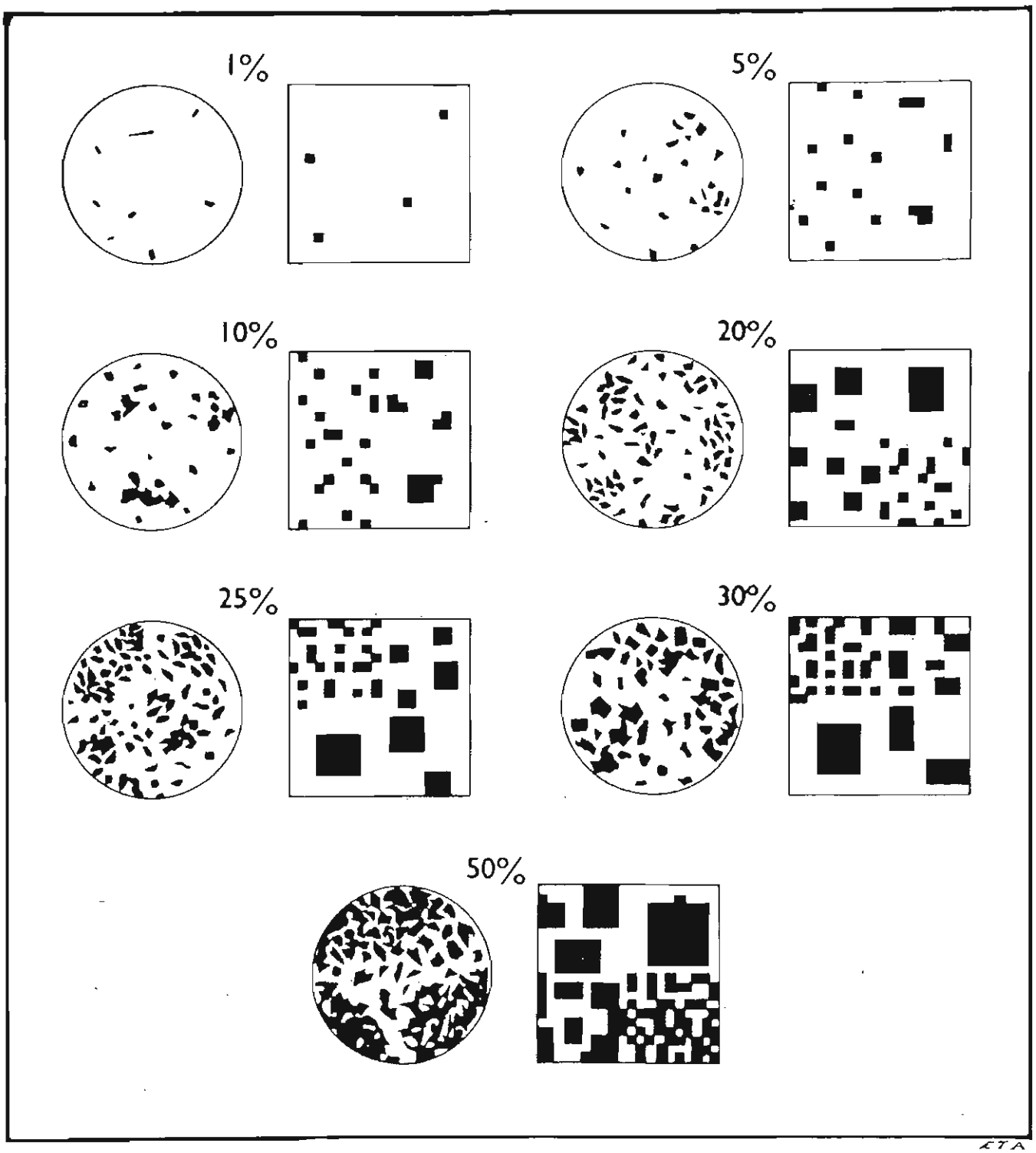
<4.0ϕ refers to all material which has passed through a 4.0ϕ (62.5μm), i.e. $x < 62.5\mu$.

>2.0ϕ refers to all material coarser than 2.0ϕ (250μ) including 1.0ϕ and 0.0ϕ fractions, i.e. $x > 250\mu$.

APPENDIX 3

PERCENTAGE ESTIMATION CHART

(compiled from Folk, 1951, and Terry and Chilingar, 1955)



APPENDIX 4

Abundance[a] and Persistence[b] of Minerals

Persistence Class	Mineral (and Hardness)		Tuhua Granite	Haast Schist	Torlesse Terrane	River-mouth	Beaches
A	Fluorapatite	(5)	***	*			
	Anatase	(5.5 - 6)	*				
	Pyrite	(6 - 6.5)	*	*	**		
	Leucoxene		**	*	***		
B	Chlorite	(1.5 - 2.5)	*	**	**		
	Muscovite	(2 - 2.5)		***	**		
	Scheelite	(4.5 - 5)		*			
	Granite Sphene	(5.5 - 6)	****			*	
C	Biotite	(2.5 - 3)	*	***	**	**	*
	Clinopyroxene	(5 - 6)	**			**	*
	Hornblende	(5 - 6)	****			**	*
D	Schist Sphene	(5 - 5.5)		***	**	***	***
	Tremolite	(5 - 5.5)		**		*	*
	Orthopyroxene	(5 - 6)					***
	Rutile	(5 - 6)		*		*	**
	Ilmenite	(5 - 6)	*	****	**	***	****
	Magnetite	(5.5 - 6.5)	****	*	*	**	*
	Epidote	(6 - 7)	***	**	***	***	***
	Garnet	(6.5 - 7.5)	*	****	**	****	****
	Zircon	(7 - 7.5)	***	*	*	**	***
	Tourmaline	(7 - 7.5)	*	**		*	*

[a] Abundances indicated by stars vary for different minerals, but for most : **** ≡ > 5% of total heavy fraction; *** = averaging 2-5%; ** = 0.2 - 2%; X = <0.2%. For ilmenite and magnetite in particular, values are likely to be greater than these figures.

[b] It is apparent from the Table that the less persistent minerals (Classes A and B) disappear down river while the more persistent minerals (Classes C and D) accumulate on the adjacent beaches.

APPENDIX 5

HF/H_2SO_4 METHOD IN DECOMPOSITION OF ILMENITE FOR AASA

From exploratory studies, the procedure outlined below was found to be most effective in decomposing a sample of ilmenite so as to leave a minimum amount of residue and lead to least subsequent precipitation of hydrolysed titanium [$Ti(OH)_4$]. Although this HF/H_2SO_4 method was not considered as suitable as bisulphate fusion, experience with it seems worth noting.

Procedure

The ilmenite was finely ground with an agate mortar. Approximately ·5 g of the powder was weighed into a platinum evaporating dish. To this, 3 ml of AR H_2SO_4 was added and the mixture agitated until the sample was thoroughly wet. Then 15 mls of 48 percent AR HF was introduced and the dish allowed to stand with occasional swirling for about half an hour. A few drops of AR HNO_3 were added and the contents were heated as strongly as possible without causing frothing on a temperature-regulated hot plate. The amount of H_2SO_4 was supplemented as required. When as little as possible of the black solid was left in the crucible, the excess HF and H_2SO_4 was fumed off. 3 ml of concentrated AR HCl were then added to redissolve the residue.

The resulting solution was then filtered through a No.4 sintered glass crucible and both the dish and crucible were rinsed with a small volume of 1 M HCl. It was then transferred to a 25 ml volumetric flask and diluted to the mark with distilled water. The collected undissolved

solids (2-5% of initial weight) was dried and its weight subtracted from the initial ilmenite weight.

Points of Note on HF/H_2SO_4 procedure

(i) Part of the collected residue was undissolved ilmenite derived from ilmenite that crept up the sides of the dish.

(ii) A minor part of it was probably insoluble basic sulphate ($TiOSO_4$) that developed from hot spots on the base of the crucible.

(iii) The use of 1 M HCl rather than water for washing was to minimise hydrohysis of titanium to $Ti(OH)_4$.

(vi) The time consuming fuming process could be hastened with the aid of an air-jet to disperse the acid fumes.

Comparison of the two Ilmenite Decomposition methods

Three samples, SW 6, SW 11 and CPM 1,were decomposed using the HF/H_2SO_4 and bisulphate fusion methods. Tabulated below are the results for chromium, nickel and copper for the sample solutions.

SAMPLE	CODE	Cr	Ni	Cu
SW 6	$KHSO_4$	71	185	75
SW 6	HF/H_2SO_4	92	164	55
CPM 1	$KHSO_4$	107	183	52
CPM 1	HF/H_2SO_4	100	118	39
SW 11	$KHSO_4$	108	183	52
SW 11	HF/H_2SO_4	109	128	41

Discussion

The chromium figures from both methods are in general agreement. But for nickel and copper the HF/H_2SO_4 gave values that are consistently lower than those from the $KHSO_4$ fusion method. A major problem with the HF/H_2SO_4 method is the complete removal of F^- from the acid/residue mixture. To ensure a better removal of F^- at least a repeat of the fuming process with the addition of more H_2SO_4 must be carried out. As this was not performed in the above test, the probable presence of F^- in the solution might have caused the consistently low values for nickel and copper. A further problem is the tendency of HF to corrode glassware.

In the HF/H_2SO_4 method, the acid fuming step is slow and it takes 3-4 hours to prepare a solution. This is unfavourable compared to the $KHSO_4$ method which takes only about an hour for each solution. The fusion method permits the direct derivation of the solution from the melt whereas in the case of the HF/H_2SO_4 method , filtering of the solutions may sometimes have to be carried out.

On the basis of the above considerations, the $KHSO_4$ fusion method is a more suitable method and hence used for all subsequent decomposition of ilmenite for analysis.

APPENDIX 6

CONCENTRATION (ppm) OF MINOR ELEMENT OF SELECTED BEACHSAND ILMENITES

Locality	Sample Code	V	Cr	Mn	Ni	Cu	Mg
Mussel Pt.B.	SW 2	733	1710	6170	261	64	3485
Carters Mill B.	SW 30	1120	1670	6940	234	68	4180
Haast B. (North side)	SW 11	516	108	11270	183	53	3270
Bruce Bay	SW 34	277	65	8270	165	48	3610
Ship CK. B.	CPM 1	462	107	12660	183	53	4370
Ross B.	SW 50	229	31	10890	1450	48	1970
Joyce Bay		415	418	12020	189	39	1820

REFERENCES CITED

BAKER, C. 1962. "Detrital heavy mineral in natural accumulates". Australasian Institute of Mining and Metallurgy, Monograph Series 1.

BRADLEY, J.P. 1977. "A study of the heavy detrital minerals of Westland". Unpublished M.Sc. thesis University of Canterbury, Christchurch.

BRADLEY, J.P.; WILKINS, C.J.; OLDERSHAW, W. and SMALE, D. 1979. "A study of detrital heavy minerals in the Taramakau Catchment". Journal of the Royal Society of New Zealand. 9:233-251.

CARPENTARIA EXPLORATION COMPANY PTY. LTD. 1971-72. Technical reports submitted to the Mines Department, Wellington. Nos. 217,218,226,235,245,253,279,318.

CARTER, L. 1975. "Sedimentation on the continental terrace around New Zealand": A review. Marine Geology. 19: 209-237.

CARTER, L. and HEATH, R.A. 1975. "Role of mean circulation, tides and waves in the transport of bottom sediments on the New Zealand continental shelf". New Zealand Journal of Marine and Freshwater Resources. 9(4): 423-448.

CARTER, L. (to be published). "Ironsand in continental shelf sediment of Westland New Zealand" - a Synopsis. (advance copy of manuscript kindly supplied by the author), N.Z. Oceanographic Institute, DSIR, Wellington.

COOPER, A.F. 1972. "Progressive metamorphism of metabasic rocks from the Haast River Group of southern New Zealand." Journal of Petrology. 13: 457-492.

COOPER, A.F. 1976. "Concentrically zoned ultramafic pods from the Haast Schist Zone, South Island, N.Z.". 19:603-623.

COOPER, A.F. and LOVERING, I.F. 1970 "Greenschist amphiboles from Haast River, New Zealand". Contribution to Mineralogy and Petrology 27:11-24.

DEER, W.A.; HOWIE, R.A. and ZUSSMAN, J. 1963. "Rock forming Minerals - non silicates". Vol. 5. Longmans, London.

FORCE, E.R. 1971. "Metamorphic source rocks of titanium placer deposits - a geochemical cycle". U.S. Geological Survey Professional Paper 959.

FURKERT, F.W. 1947. "Westport Harbour". Transactions of the Royal Society of New Zealand. 76(3): 373-402.

GJELSVIK, T. 1957. "Geochemical and mineralogical investigation of titanoferous iron ores, West Coast of Norway". Economic Geology 52: 482-498.

GOVETT, G.J.S. and WHITEHEAD, R.E. 1973. "Errors in atomic absorption of Pb, Zn, Ni and Co in geologic materials". Journal of Geochemical Exploration. 2:121-131.

HUTTON, C.O. 1950. "Studies on heavy detrital minerals". Geological Society of American Bulletin. 61:635-716.

LOVELOCK, B. 1978. "First-row transition elements in the magnetise of Westland beachsands ". Unpublished B.Sc. (Hons) project report, University of Canterbury, New Zealand.

LISTER, G.F. 1966. "Selected iron-titanium deposits". Economic Geology. 61:275-310.

MARSHALL, T.: SUGGATE, R.P. and NICHOLSON, D.S. 1958. "A borehole survey of ilmenite-bearing beach sands at Cape Foulwind, Westport". New Zealand Journal of Geology and Geophysics. 1(2):318-324.

MASON, B.H. 1962. "Metamorphism in the Southern Alps of New Zealand". Bulletin of the American Museum of Natural History. 123(article4): 211-248.

MASON, B.H. 1966. "Principles of Geochemistry", 3rd edn., Chapter 10. 248-281; Wiley, New York.

MASON, B.H. and TAYLOR, S.R. 1955. "The petrology of the Arahura and Pounamu series in the Kokatahi River, North Westland". Transactions of the Royal Society of New Zealand. 82: 1061-1070.

MARTIN, W.R.B. 1955. "The iron and titanium ores of New Zealand". N.Z. Engineering. 10(10): 317-336.

McPHERSON, R.I. 1978. "Geology of quaternary ilmenite - bearing coastal deposits at Westport". New Zealand Geological Survey Bulletin N.S. 87.

MUTCH, A.R. and McKELLAR, I.C. 1964. Sheet 19, Haast (1st edn.), Geological Map of New Zealand. 1:250,000 Department of Scientific and Industrial Research, Wellington, New Zealand.

NICHOLSON, D.D. 1967. "Distribution of economic minerals in South Island, West Coast sand". New Zealand Journal of Science 10(2): 447-456.

NICHOLSON, D.D.: CORNES, J.J.S. and MARTIN, W.R.B. 1958. "Ilmenite deposites in New Zealand". New Zealand Journal of Geology and Geophysics. 1(4):611-616.

O'SHAUGHNESSY, P.T. 1973. "Determination of trace levels of chromium in ilmenite by atomic absorption spectroscopy". Analytical Chemistry 45: 1946-7.

READ, H.H. 1970. "Rutleys element of mineralogy", 26th edn., Thomas Murby and Co., London.

REED, J.J. 1958. "Regional metamorphism in south-east Nelson". New Zealand Geological Survey N.S. 60.

RINGWOOD, A.E. 1955. "The principles governing trace element distribution during magmatic crystallisation. Part 1: The influence of electronegativity". Geochimica et Cosmochimica Acta. 7: 189-202.

SEARS, G.W. and QUILL, L. 1925. "Critical Studies on the fusion of rare-metal ores. I. The pyrosulphase fusion of titanium ores". Journal of American Chemical Society. 47:922-929.

SMALE, D. and NATHAN, S. 1980. "Heavy minerals in pre-tertiary rocks of the Paparoa Range, West Coast South Island", NZGS Report G36. Department of Scientific and Industrial Research, Christchurch.

TAYLOR, S.R. 1955. "The origin of some New Zealand metamorphic rocks as shown by their major and trace element composition". Geochimica et Cosmochimica Acta. 8:182-197.

TURNER, F.J. 1933. "The metamorphic and intrusive rocks of South Westland". Transactions of the New Zealand Institute 63:178-284.

GUYON, W. 1967. Sheet 17, Hokitika (1st edn) Geological Map of New Zealand 1:250,000 Department of Scientific and Industrial Research, Wellington, New Zealand.

WELLMAN, H. W. and WILLET, R.W. 1942. "The geology of the West Coast from Abut Head to Milford Sound - Pt 1. Transactions of the Royal Society of New Zealand". 71: 282-306. Pt. 2. Ibid. 72:199-219.

WENTWORTH, C.K. 1922. "A scale of grade and class terms for clastic sediments". Journal of Geology 30:377-392.

OTHER REFERENCES CONSULTED

This list comprises relevant background reference material, but which is not cited directly in the thesis.

ANGINO, E.E. and BILLING, G.K. 1972. "Atomic absorption spectrometry in geology". 2nd edn.; Elsevier, New York.

BASTA, E.Z. 1959. "Some mineralogical relationship in the system Fe_2O_3-Fe_3O_4 and the composition of titanomaghemite". Economic Geology 54:698-719.

BELL, J.M. 1905. "The Geology of the Hokitika sheet North Westland quadrangle". New Zealand Survey Bulletin N.S. 1.

BORISENKO, L.F. and POLKANOV, Yu.A. 1976. "Vanadium in ilmenite of Diverse origin". Doklolad Sci. USSR Earth Sci. Sect. (Washington D.C.) 221(1-6):239-242.

CARR, M.H. and TUREKIAN, K.K. 1962. "Chromium in granite rocks". Geochimica et. Cosmochimica Acta 26:411-415.

CURTIS, C.D. 1963. "Application of the crystal-field theory to the inclusion of trace transistion elements in minerals during magnetic differentiation". Geochimica et. Cosmochimica Acta 28:289-303.

DUNCAN, A.R. and TALYOR, S.R. 1968. "Trace element analysis of magnetites from andesitic and dacitic lava from Bay of Plenty, New Zealand". Contrib. Mineral. and Petrol. 20:30-33.

FISHER, R.P. 1975. "Vanadium resources in titanoferous magnetite deposits" U.S. Geological Survey. Professional Paper 926-B.

FORMINYKH, V.G. and YAROSH, P.Y. 1977. "Chromium in ural magnetite". Geochem. Inst. (Washington, D.C.) 14(5):50-56.

FURMAN, N.H. 1939. "Scott's Standard Methods of Chemical Analysis", 5th edn.; Titanium, 975-1000. D.Van Nostrand company, Inc. New York.

GRYS, A.O. 1970. "Copper and Zinc in alluvial magnetites from Central Ecuador". Economic Geology 65:714-717.

ISAACS, T. 1963. "Theories of lattice substitions". Nature. 198:1160-1.

KISVARSANYI, G. and PROCTOR, P.D. 1967. "Trace element content of magnetise and hematite, Southeast Missouri iron metallogenic province, U.S.A." Economic Geology 62:449-472.

JAMES, A.H. and DENNEN, W.H. 1962. "Trace ferrides in magnetite ores of Mt. Hope mine and North Jersey Highland". Economic Geology 57:439-449.

MERCY, E. and O'HARA, M.J. 1967. "Distribution of Mn, Cr, Ti, Ni, in co-existing minerals of ultramafic rocks". Geochimica et Cosmochimica Acta 31:2331-2341.

MORGAN, P.C. 1980. "The geology of the Mikonui subdividion North Westland". New Zealand Geology Survey Bulletin n.s.6.

NATHAN, S. 1975. "Late quarternary terraces between ship Creek and the Whakapohai River, South Westland New Zealand". Journal of the Royal Society New Zealand. 5:313-327.

NICHOLSON, D.S., SHANNON, W.T. and MARSHALL, T. 1966. "Separation of ilmenite, zircon and monazite from Westland Beach sands". New Zealand Journal of Science. 9:586-598.

NICOLLET, C. and ANDRIANBOLOLONA, D.R. 1980. "Distribution of transition elements in crustal metabasic igneous rock". Chemical Geology. 28:79-90.

SOHOCK, H.H. 1979. "Distribution of rare-earth and other trace elements in magnetite". Chemical Geology. 26:119-183.

SILL, C.W. 1976. "Problems in sample treatment in trace analysis". Natural Bureau of Standards Special Publication 422. Proceedings of the 7th IMR Symposium, Gaithersbury, Maryland.

STUEBER, A.M. and GOLES, G.G. 1965. "Abundances of Na, Mn, Cr, Sc and Co in ultramafic rocks". Geochimica et Cosmochimica Acta. 31:75-93.

SULCEK, Z.; PAVANDRA, P. and DOLEZAL, J. 1977. "Decomposition procedures in inorganic analysis". CRC Critical Reviews in Analytical Chemistry. 6:255-323.

UYTENBOYAARDT, W. and BURKE, E.A.J. 1971. "Tables for microscopic identification of ore minerals". 2nd edn., Elsevier, New York.

WAGER, L.R. and MITCHELL, R.L. 1951. "The distribution of transition elements during strong fractionation of basic magma". Geochimica et Cosmochimica Acta. 1:129-208.

WILLIAMS, G.J. 1974. "Economic Geology of New Zealand". Australiasian Institute of Mining and Metalurgy, Monograph series 4.

WRIGHT, J.B. 1963. "Iron-titanium oxides in some New Zealand iron sands". New Zealand Journal of Geology and Geophysics. 7:424-444.

WRIGHT, J.B. and LOVERING, J.F. 1965. "Electron-probe micro-analysis of the iron-titanium oxides in some New Zealand iron sands". Mineralogical Magazine. 35:604-621.